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Direct Reduction Processes
For the Production of
Titanium Metal

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Direct Reduction Processes

for the

Production of Titanium Metal

Report of

The ad hoc Panel on Direct Reduction Processes

for the Production of Titanium Metal

of the

Committee on Technical Aspects of

Critical and Strategic Materials

National Materials Advisory Board

Division of Engineering -- National Research Council

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This study by the National Materials Advisory Board was conducted under Contract No. GS--00-DS- (P)-94008 with the General Services Administration on behalf of the General Services Administration, the Office of Emergency Preparedness, and the Department of Commerce. Partial support of this contract was provided by the U. S. Bureau of Mines.

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PREFACE

This study, Direct Reduction Processes for the Production of Titanium Metal, was performed by an ad hoc Panel of the National Materials Advisory Board (NMAB) Committee on Technical Aspects of Critical and Strategic Materials. The parent Committee is a steering group that responds to the requests of its sponsors, the General Services Administration and the U. S. Bureau of Mines, and that assesses the implications of technological change and usage trends on the supply/demand balance in applications utilizing various essential materials from the viewpoint of necessary civilian needs and military requirements.

The Panel included members from academia, industry, and government. To meet its objectives, the Panel was divided into the following four subpanels:

Introduction: K. B. Higbie

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ABSTRACT

Existing technology was reviewed with the aid of individuals currently* and formerly associated with the titanium metal industry. Reduced demand for titanium metal after 1957 adversely affected the titanium metal producing industry in the United States. Currently, of the titanium metal consumed domestically, 30 percent is imported. The domestic producers, as well as the major foreign producers, use the Kroll (magnesium) or Hunter (sodium) technology developed in the United States. The development of new technology to produce pure titanium metal at a lower cost is important because of (1) economic aspects of commercial markets, and (2) strategic aspects of domestic production. While no essentially new technology appears imminent, areas for development in research and production are identified. Process improvements are needed if titanium, relative to other metals, is to attain an improved competitive position for large tonnage use.

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* The data and assumptions presented in this report are based on information obtained through September 1973.

I. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

A. Conclusions

1. Present technology, exemplified by the Kroll (magnesium reduction) and Hunter (sodium reduction) processes, can produce metal of adequate purity for current domestic use.

2. Current sales-price data indicate that domestically produced titanium does not compete with imported titanium, although this situation appears to be improving.*

3. Some improvements in the Kroll Process technology have occurred during recent years; however, it remains a batch process and, apparently, is not adaptable readily to continuous operation.

4. Of the two currently used processes, the Hunter is considered to have the better potential for continuous operation.

5. Electrolytic reduction reportedly has the potential to reduce costs;** however, major technological improvements are needed.

6. In the future, direct ingot production may offer a major cost in reduction over making sponge, which requires further energy input for consolidation. Since a significant portion of the cost of finished titanium products is associated with processing following sponge production, processes involving molten titanium are of continuing interest and merit further attention for long-range development.

7. Several concepts that could lead to production of high-purity titanium metal are in early stages of development, but sufficient laboratory data are not available from which adequate inferences can be drawn.

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* As of fall 1973, domestic producers were able to market their titanium production.

** Although limited data were available on process costs for present technologies, the Panel was unable to obtain cost information on alternate technologies that would permit economic comparisons.

8. Materials of construction are a major design limitation to achieving success with new processes. Existing construction materials apparently are adequate for the production of commercial sponge by present Kroll and Hunter technologies.

9. Although limited data were available on process costs for present technologies, the Panel was unable to obtain cost information on alternate technologies that would permit economic comparisons.

B. Recommendations

1. Further modification of current reduction techniques should be investigated to reduce production costs.

2. Research and process development should be undertaken on present production techniques (particularly sodium reduction) to provide greater process continuity without increasing cost or sacrificing metal purity. Although the operating costs for continuous processing are generally less because of decreased labor content, process savings may be nullified by increased capital investment.

3. Further research and development engineering should be undertaken to improve electrolytic reduction processes. Design and construction of diaphragms with long service lives are essential to the process.

4. The technology and improved materials required to handle high-temperature molten phases in continuous processes should be developed so that a process could lead directly from purified feed material, such as the chloride, to titanium or titanium-alloy mill products.

II. INTRODUCTION

A. Statement of Problems

Titanium metal is strategically important for the defense of this nation, and a competitive and viable industry must be maintained to assure a continued supply. For economic reasons, however, the nonintegrated titanium processing and fabrication industry has been increasing its dependence upon imported sponge metal. If the domestic industry could produce high-quality sponge or metal (particularly low in O_2, N_2, Cl_2, Na, and Mg) at lower costs, U.S. titanium markets could expand greatly and, thus, support a bigger, more viable and competitive domestic industry. The net result would be the preservation of the U.S. titanium industry as part of the defense base. Accordingly, the National Materials Advisory Board undertook this study at the request of the U. S. Bureau of Mines, the General Services Administration, and the then existing Office of Emergency Preparedness. The purpose of the study was to assess the potential of new technology for producing pure titanium metal in the near future.

Known and probable paths for the extraction and purification of titanium, leading from impure TiO_2 to pure titanium crystals, have been presented by Henrie (1965)[*] in a useful graphical form, (Figure 1) and this diagram was used as a guide by the Panel in its examination of existing processes and extrapolation to probable new processes. The data and assumptions in this report are based on information available in the literature and on personal presentations to the NMAB Panel through September 1973.

B. Historical Background

The existence of titanium, a relatively new metal that did not become available in commercial quantities until after World War II, was discovered by William Gregor in 1790, but almost one century passed before Berzelius

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[*]An alphabetical list of references appears at the end of each chapter.

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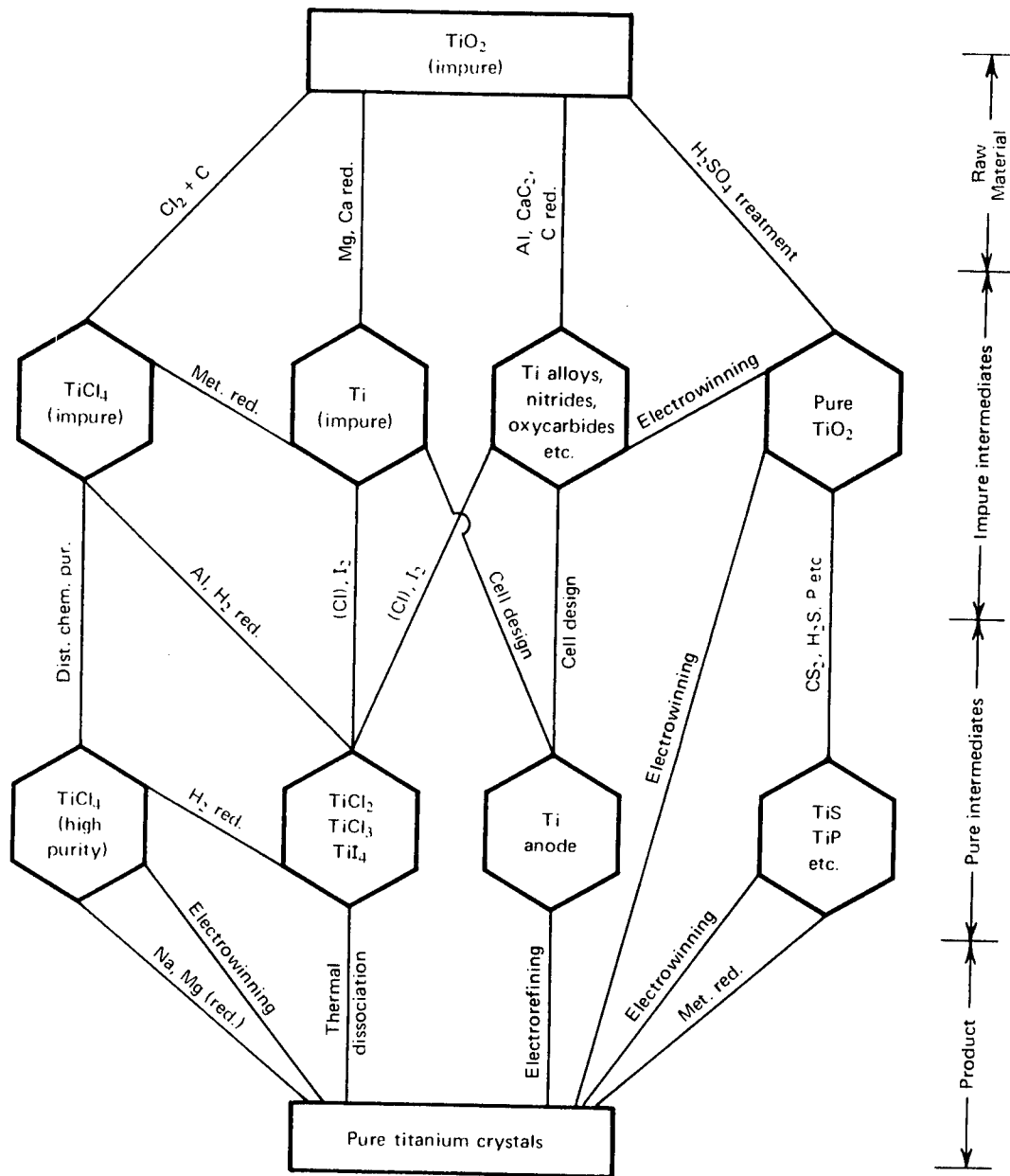
FIGURE 1. Possible routes for titanium processing (Henrie, 1965).

produced the first in 1876. This metal was prepared by reducing potassium fluotitanate with potassium metal and was relatively impure, and was metal produced in 1887 by Nilson and Petterson who reduced titanium tetrachloride with sodium.

In 1910, Hunter produced the first "pure" titanium by repeating the experiments of Nilson and Petterson using a higher purity tetrachloride feed (Hunter, 1910). The metal was ductile when hot but brittle when cold. In 1925, the first fully ductile (hot or cold state) titanium was prepared by decomposing titanium tetraiodide on a hot tungsten filament (van Arkle and deBoer, 1925). In 1937, W. J. Kroll credited with developing the technology that led eventually to the large-scale commercialization of titanium metallurgy invented the magnesium reduction process (reducing titanium tetrachloride with magnesium) by utilizing an inert argon atmosphere to protect the titanium metal from reoxidizing (Kroll, 1955). This breakthrough permitted the production of 99 percent pure metal. Most of the commercial production of titanium metal in the world has been based on either the Kroll (magnesium) or Hunter (sodium) process.

During the past 35 years, the U.S. government extensively financed the development of technology for quantity production of the metal. In 1938, the U.S. Bureau of Mines began to look at various technologies for making the metal and eventually concentrated its effort on developing the Kroll process. A pilot production facility was built in 1942 at the Bureau's Boulder City, Nevada, station. This unit ultimately validated Kroll's technology and provided much of the basic information upon which the commercial industry developed. In 1947, the first 2 tons of sponge metal produced in the United States were made by the Bureau of Mines.

In 1948, E. I. dePont de Nemours and Co. built the first nongovernment pilot plant. That year is considered the start of small-scale commercial production of titanium metal sponge, and a total of 10 tons of metal was produced from all sources. Production increased slowly until 1952, when du Pont's daily output averaged 2.5 tons of sponge metal and the entire industry produced 1,075 tons.

Further government aid, in the form of contracts with the Defense Materials Procurement Administration (DMPA) and the General Services Administration (GSA) later encouraged additional growth of the industry. Early in 1950, the National Lead Co. and Allegheny Ludlum Steel Corp. organized the Titanium Metals Corp. of America and leased a then-government-owned magnesium plant at Henderson, Nevada, to adapt the Bureau of Mines-developed Kroll technology to the facility. The new company obtained a DMPA contract in 1951 and was in full production (3,600 short tons of titanium sponge per year) by 1954.

In 1953, other DMPA contracts were awarded to Cramet Inc., a subsidiary of the Crane Co., and the Republic Steel Corp. to construct a 6,000 ton-per-year titanium-sponge plant at Chattanooga, Tennessee. This plant started operating in the spring of 1955, utilizing the Kroll process. In 1954, a Dow Chemical Co. contract from the General Services Administration permitted the expansion of Dow's pilot-plant capacity to 1,800 tons per year. The Electro Metallurgical Co., a division of Union Carbide Corp. also received a government contract in 1954 to build and operate a titanium metal plant in Ashtabula, Ohio. This plant was to produce 7,500 tons of sponge metal per year by a sodium reduction technique. In this same year, the Foote Mineral Co. produced 250 pounds of titanium metal in a small pilot plant utilizing the iodide method.

By early 1955, the United States was the world's leading producer of titanium metal. At that time, Japan, utilizing the Kroll process, was the only other country known to make the metal on a commercial scale.

In 1956, U. S. Industrial Chemical Co., a division of National Distillers, Inc., announced plans to build a 5,000-ton sponge plant in Ashtabula, Ohio. During construction of the plant, U. S. Industrial chemical Co. joined Mallory Sharon Titanium Corp. (a titanium fabricator) to form the Mallory Sharon Metals Corp.; later, this firm was renamed Reactive Metals, Inc., and still later became known as RMI Corp.

The rapid growth of the titanium industry between 1950 and 1957 (illustrated by Figure 2) resulted largely from the government's urgent demand for titanium metal for use in manned high-speed aircraft. This picture changed drastically in 1957-58 when the government decided to base its defense upon missles rather than manned aircraft. Consequently, the government reduced its contracts to purchase titanium metal and several new firms ceased operations almost as soon as their sponge plants were planned or brought into full production. *

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* For example, 1956 Allied Chemical and Dye Corp. and Kennecott Copper Corp. announced a joint venture, the Allied Kennecott Titanium Corp., that would involve building a 5,000-ton per year titanium plant utilizing a new continuous reduction process. The plant was never built, and the Panel was unable to obtain data on the technology. In 1957, Columbia-Southern Chemical Co. and Imperial Chemical Industries also were on the verge of building a 5,000-ton sponge plant (believed to be a sodium reduction facility) if given some governmental assistance, however they changed their plans with the reversal of the titanium market (although Imperial did construct a small plant in England).
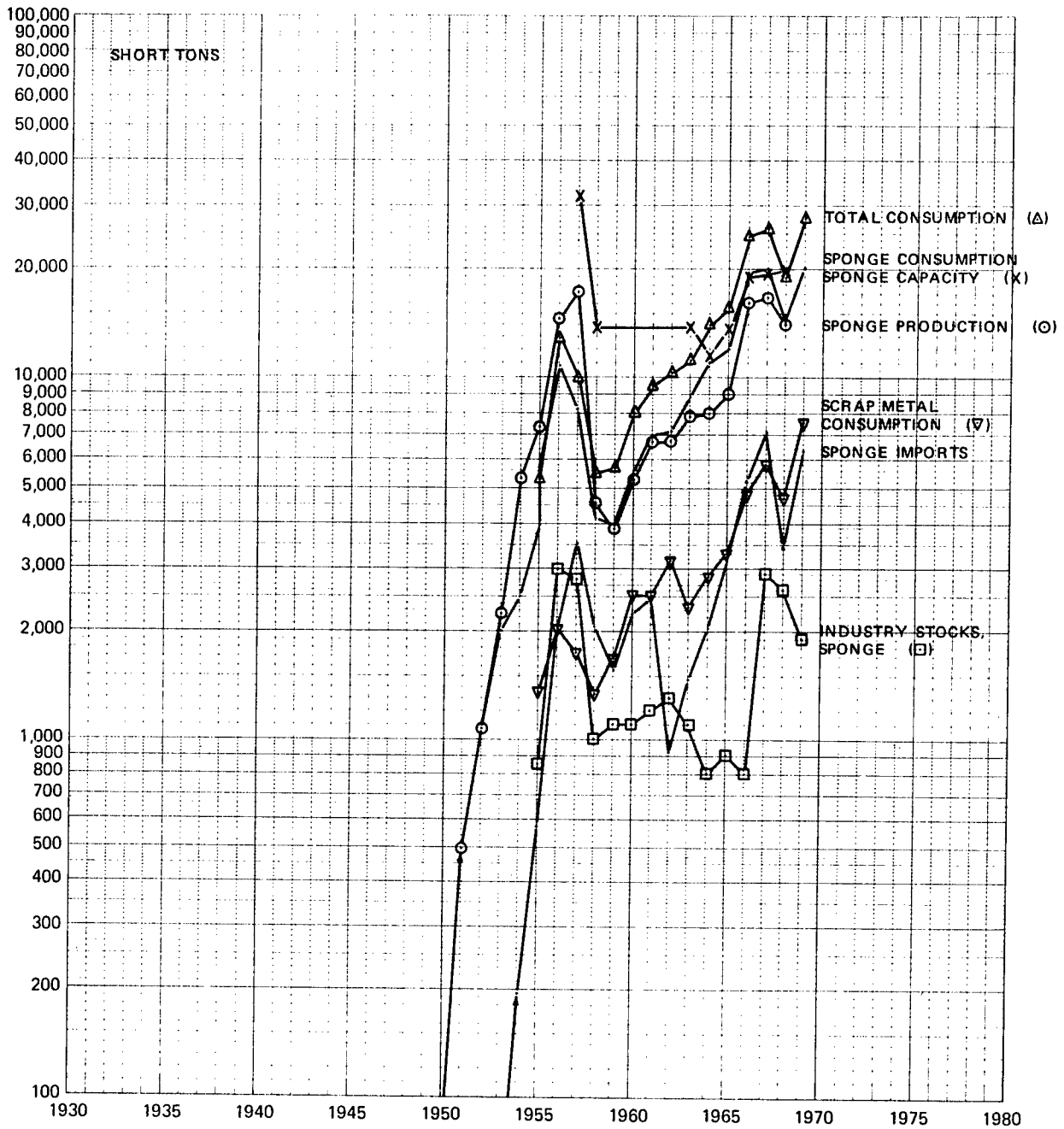
FIGURE 2. Titanium metal: Salient statistics, 1950-69 (Stanford Research Institute)

By 1960, only three major producers remained: Titanium Metals Corp. of America, E. I. du Pont de Nemours and Co., and Reactive Metals, Inc., and by 1962, du Pont ceased titanium production. The first two firms employed the Kroll process and the latter employed the Hunter process.

Electrolytic processes were the only other reduction processes that potentially were capable of producing quality titanium metal at a price competitive with the magnesium and sodium reduction methods. Prior to the drastic titanium market change in 1957, several firms explored various aspects of electrolytic technology but none of the processes was developed sufficiently to warrant commercialization. Since 1957, Titanium Metals Corporation of America has built and operated a small pilot commercial electrolytic sponge production facility. Its product was sold on the open market at premium prices because of the extra high purity of the electrowon product (Minkler, 1973).

In 1966, a titanium melter, Oregon Metallurgical Corp. (OREMET) began construction of a titanium reduction facility in Albany, Oregon, to provide a more integrated operation. Kroll technology was utilized in the new operation that was designed to produce 625 tons a year.

In view of their dependence on the growth of the aerospace industry and upon government stockpile programs, abandonment of the supersonic transport (SST) project in 1971, the exceedingly slow development of military and commercial aviation programs, and the availability of lower cost Japanese and Soviet sponge created serious problems for the domestic titanium suppliers during the second half of 1971, three producers closed their reduction facilities for various lengths of time.*

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* One had not restarted its reduction plant by January 1974.

In mid-1973, the Howmet Corp. and Dow Chemical Co. announced plans to scale up an electrolytic method for making titanium metal. Dow developed the process by following some early work by the U.S. Bureau of Mines in Boulder City, Nevada, but the actual production facility is not expected to be constructed for several years.

Table I summarizes the growth of the titanium sponge metal industry since 1951 (domestic production figures since 1964 are withheld because of the difference in size of the three producers). As can be seen, consumption of titanium sponge reached its highest level in 1969 prior to congressional discussions that halted the SST program. Imports of sponge between 1956 and 1961 were largely for the government's stockpile program. However, since 1962, low-priced foreign sponge imports slowly have increased their share of the market from 6 percent in 1962 to about 40 percent in early 1973.** Table II presents worldwide titanium metal production capacity in 1973 and indicates the type of reduction technology employed.

** As 1973 ended, two U.S. sponge-producing plants were operating at maximum production levels commensurate with the supplies of chlorine and electricity; imports of sponge metal were decreasing because of decreasing Soviet exports and reduced Japanese production resulting from the energy crisis.

TABLE 1. Titanium Sponge Statistics (in short tons): 1951-1972 (U.S. Bureau of Mines)

Year	Domestic Sponge			Foreign Sponge			Total Apparent Consumption	Import Use Percent of Apparent Consumption
	Quanity Produced	Placed in Stockpile	Industry Use*	Total Imports	Placed in Stockpile	Industry Use*		
1951	495	—	n.a.	n.a.	n.a.	n.a.	n.a.	—
1952	1,075	113	962	n.a.	n.a.	n.a.	n.a.	—
1953	2,241	313	1,928	157	—	157	n.a.	—
1954	5,370	2,277	3,093	193	—	193	n.a.	—
1955	7,398	3,901	3,497	567	—	567	n.a.	—
1956	14,595	2,712	11,883	2,048	1,080	968	10,936	9
1957	17,249	10,505	6,734	3,532	1,316	2,216	8,221	27
1958	4,585	2,642	1,943	2,073	1,645	428	4,147	13
1959	3,898	13	3,885	1,563	1,355	208	3,953	5
1960	5,311	---	5,311	2,231	1,395	836	5,487	15
1961	6,727	---	6,727	2,490	1,755	735	6,991	10
1962	6,730	---	6,730	925	475	450	7,136	6
1963	7,879	---	7,879	1,468	---	1,468	8,865	17
1964	withheld	---	withheld	2,056	---	2,056	11,131	18
1965	"	---	"	3,134	---	3,134	12,105	26
1966	"	---	"	5,675	---	5,675	19,177	30
1967	"	---	"	7,144	---	7,144	20,062	36
1968	"	---	"	3,443	---	3,443	14,237	24
1969	"	1,006	"	6,332	---	6,332	20,124	31
1970	"	4,277	"	6,543	---	6,543	16,414	40
1971	"	---	"	3,023	---	3,023	12,145	25
1972	"	847	"	3,965	---	3,965	13,067	30
1973**	"	2,544	"	6,700	---	6,700	19,300	35

* Domestic production or total imports less quantity placed in government stockpile.
** Preliminary U.S. Bureau of Mines figures.

TABLE II. Plants for the Production of Titanium Sponge (U.S. Bureau of Mines).

	Type	Capacity (millions of lb/year)
United States:		
TIMET	Mg	28
RMI	Na	15
OREMET	Mg	5
England:		
ICI	Na	8
Japan:		
Toho	Mg	10
Osaka	Mg	10
New Metals	Na	4
Soviet Union:		
3	Mg	60

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III. CURRENT TECHNOLOGY (COMMERCIAL)

In 1973, domestic commercial production of titanium metal was achieved using three different technologies: (1) the Kroll process that uses magnesium as the reducing agent for titanium tetrachloride, (2) the Hunter process that employs sodium as the reducing agent for titanium tetrachloride, and (3) an electrolytic technique in which titanium tetrachloride is reduced electrically to titanium metal and chlorine gas. The latter technology is employed only on a scale comparatively smaller than the first two.

Generally, Japanese and Soviet titanium producers use the Kroll process to manufacture the bulk of their titanium metal. Both Japanese and Soviet producers use vacuum distillation to remove chlorides and other volatile impurities rather than leaching or gas-sweeping operations. Recently, a small, new Japanese titanium sponge producer, New Metal Products Co., began using the Hunter (sodium reduction) process and water leaching to reduce the residual salt content of the sponge. The titanium sponge from this new plant is identical, by all physical and chemical tests, to the sponge produced by RMI.

Titanium tetrachloride, employed as the starting chemical for all three production technologies, is obtained commercially from the chlorination of the mineral rutile. With the resources of this material dwindling throughout the world, several new chemical systems have been developed for making synthetic rutile or rutile substitutes from ilmenite or other abundant titanium bearing minerals. These new products eventually may play a larger role in providing the starting material for titanium tetrachloride production (NMAB, 1972).

A. <u>The Kroll Process</u>

Dr. W. J. Kroll (1955) first attempted, as early as September 1930, to
reduce $TiCl_4$ with sodium by the Nilson and Petterson method (called the
Hunter process in the United States), in which, clean sodium lumps are sub-
merged in pure titanium tetrachloride and reacted in a pressure vessel.
He found, however, that the sudden reaction of all the reagents built up a
considerable pressure that frequently ruptured the reaction vessel and, after
numerous apparatus failures, tried a reaction method at essentially atmo-
spheric pressure in which the titanium tetrachloride was added at a slow rate
so as not to generate high temperatures or excessive pressures. The reduc-
ing agent was protected by an atmosphere of argon or helium. At first,
calcium was used as a reducing agent, but on July 30, 1937, Kroll switched
to magnesium as the reducing agent using the same equipment. This pro-
cedure was the basis of the 1940 U. S. Patent 2,205,854. The first claim
of the patent is: "The method of producing cold-malleable titanium consist-
ing in causing a halide of titanium to chemically react with an alkaline earth
metal at an elevated temperature below the boiling temperature of said
metal and in the presence of a protective gas while maintaining normal
pressure." Thus, the net chemical reaction is: $TiCl_4 + 2Mg = Ti + 2MgCl_2$.

The reaction is highly exothermic (-206 Kcal/mole at $900\,^{\circ}C$). The free
energy is -76.2 Kcal/mole at $900\,^{\circ}C$ so that back reactions are minimal,
permitting and maintaining essentially complete reaction even during cooling.
Heat is added during the later stages of the process to maintain favorable
kinetics.

Because the temperature of the process is far below the melting point
of the titanium, a "sponge" forms on the sides and the bottom of the
reaction vessel. The "sponge" varies from almost solid material to loose

dendritic growths. The magnesium chloride fills the pores of the metal and surrounds individual pieces and particles; the center of the vessel is filled chiefly with the chloride. Also, a surplus of magnesium exists in the reaction mass because a greater than stoichiometric quantity is used to assure complete reduction of the titanium tetrachloride and because magnesium is slightly soluble in titanium.

1. Present Status

Present day commercial production of titanium by the Kroll process centers about the technology developed in the early 1950s by the Bureau of Mines at its pilot plant in Boulder City, Nevada. The basic process was published in 1952 and can be described briefly as follows: After a weighed amount of clean magnesium is placed in a cylindrically shaped steel pot, the lid is welded. The atmosphere in the pot is evacuated and then backfilled with helium. Next, the pot is placed in a furnace and heated until the magnesium begins to melt. Titanium tetrachloride is added at a predetermined rate and the outside pot temperature is held between 750 and 800 $^\circ$C. Since the reaction is highly exothermic, the rate of addition of the tetrachloride is regulated to control the temperature. Provision is made for passing the tetrachloride through a feed pipe in the cover plate. Inlet and outlet pipes for the inert gas pass through this cover plate. A safety valve is inserted in the gas line to relieve the pressure of tetrachloride build-up if the reaction stops for any reason. The magnesium chloride produced is removed as a liquid by tapping several times during the batch operation. After completion of the reaction, the pot is removed from the furnace and cooled. The pot then is opened in a room with very dry atmosphere and the products are removed from the pot by cutting the reaction mass out on a large lathe. The titanium chips are collected in a basket and heated in a

vacuum furnace under 40 microns absolute pressure at 910°C or higher to volatilize the unused magnesium and resultant magnesium chloride that are condensed in a water-cooled retort.

While the basic technology has not changed since the initial Bureau of Mines development, many minor changes have been made. The seal between the reaction chamber and the lid now is made with ring seals rather than a permanent weld. The technique for removing the final sponge is critical since the purity of the metal varies with the location at which it is formed. Metal close to the walls of the reactor has a higher impurity content, particularly iron, than the remainder of the deposited titanium, because the magnesium participating in the latter stages of the reaction passes over and gives up its impurities to the first deposits of titanium. The Bureau of Mines found that vacuum distillation of the impure sponge readily removed the volatile magnesium impurities; however, some titanium producers chose to leach the sponge rather than install the expensive vacuum pumping installations that were troublesome and required extensive protection from attack by the volatile titanium chlorides produced during the reaction. Also, the development of a small air leak in the reactor could destroy very readily the entire batch of material. Distillation was a very slow process, sometimes taking as long as 48 hours to treat a 200-pound batch of titanium. Now, commercial batches are 3,000 to 4,000 pounds in size.

The successful melting procedure that finally evolved was: (a) to press the titanium sponge into a shape suitable as a consumable electrode in a vacuum arc melting furnace; and (b) to operate the furnace so that the consumable electrode melts away and the molten titanium forms an ingot, 6 to 14 inches in diameter, in the lower water-cooled electrode. For larger sizes, better quality, and alloying, the first ingot is remelted in a

similar fashion; this is the so-called double-melting technique. As mentioned above, cleaner sponge could be made by vacuum distilling the chloride and excess magnesium rather than by leaching; however, the same effect is achieved if vacuum pumps are used during the arc melting process to draw off any vapors of chloride and magnesium left by incomplete leaching.

2. Improvements

The newest modification to the Kroll process, on a production basis, is the Oregon Metallurgical Corporation (OREMET) inert gas sweep (Peters, 1973). In this modification, a horizontal reactor (22 feet in length and 6 feet in diameter) capable of holding approximately 13,000 to 14,000 pounds of sponge is used.

The cycle is started by bringing the retort to temperature, purging with inert gas to prevent oxidation of the magnesium, and then adding 16,000 to 17,000 pounds of molten magnesium. The added magnesium is 25 percent in excess of stoichiometric requirements. The loaded retort is heated to approximately 800°C. Titanium tetrachloride is sprayed into the reactor at a rate that is governed by the temperature of the retort which, as a result of the exothermic reaction, is kept in the 850° to 920°C range. At a given point in the reduction cycle, the first tap of magnesium chloride is made. Through tapping and reduction cycles, the tapped quantities are adjusted so that the level of molten magnesium surface ranges from the level of a grid installed about 12 inches above the bottom of the reactor to about 24 inches above the grid. Additional charges of titanium tetrachloride and tapping of magnesium chloride are made until the required quantity of 46,000 to 47,000 pounds of titanium tetrachloride has been added. Once this is accomplished, a soak period is provided to allow completion of the reaction and separation of excess magnesium and residual magnesium chloride from the sponge.

At this point in the process, approximately 14,000 pounds of titanium sponge is in the form of a cake on top of the grid, 46,000 pounds of magnesium chloride have been tapped, and about 3,000 pounds of magnesium chloride remain in the sponge mass to be removed by a slow sweep of helium at about 1000 °C (the 3,000 pounds would not be readily recovered except by a vacuum distillation or inert gas sweep, and no leaching is used in the OREMET process). By exerting a slight mechanical pressure on the bottom of the grid, the cake of sponge is separated from the retort and removed readily. Selective sectioning of the large cake permits recovery of substantial amounts of high-purity sponge (Peters, 1973).

To summarize, the advantages of the OREMET process are (Peters, 1973):

a. Individual batch sizes of 13,000 to 14,000 pounds as contrasted with the customary 2,000 to 4,000-pound batch

b. Removal of residual magnesium chloride and magnesium by an inert gas sweep rather than vacuum distillation with its high equipment cost

c. High recovery of magnesium chloride for recycling back as magnesium and chlorine with attendant environmental benefits

d. Possible energy savings by charging liquid magnesium to the reduction reactor and recovering liquid magnesium chloride electrolytic cells.

3. Economics

The actual cost of titanium sponge production is not determined readily, but it is well known that domestic producers have been unable to compete with low-priced imports. Based on data presented to the Panel (Peters, 1973), Table III presents sponge production cost breakdowns by both process step and cost component. As is indicated, the major cost factor is the production of titanium tetrachloride and 55 percent of the cost of titanium

TABLE III. Estimated Sponge Production Costs,* Kroll Process (percent of total cost).

By Process Step	1972	1967
Production of titanium tetrachloride	38	25
Reduction to sponge	35	41
MgCl$_2$ recycle	27	34
Total	100	100

By Cost Component	1972	1967
Labor	26.0	
Supervision	5.5	65.5
Maintenance	26.5	
Utilities	17.0	9.7
Raw material	25.0	24.8
Total	100.0	100.0

(Labor, Supervision, and Maintenance for 1967 are bracketed together as 65.5)

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* Depreciation excluded.

tetrachloride is represented by the cost of rutile. The price of rutile has increased steadily so that, as of spring 1973, it was quoted on the West Coast at between $200 and $220 per ton, which is equivalent to $0.20 to $0.21 per pound of titanium sponge at about 90 percent recovery.

The total energy requirements of the actual commercial reduction processes are not available; however, estimates including magnesium reduction technology have been made of the energy required to make titanium from various TiO_2-bearing raw materials (Bravard et al., 1972). Equivalent coal energy requirements for the production of titanium metal are shown in Table IV to vary from 126,115 kwh per ton of titanium from rutile. As the TiO_2 content of the ore is reduced or the nature of the ore changes, the equivalent coal energy requirement increases and is estimated to be 206,075 kwh per ton for soil deposits. It can be seen that the production of titanium is heavily dependent on electricity which represents 55 percent of the total energy requirement. No data were found that would indicate if the direct electrowinning of titanium from fused salt baths might result in a saving of electrical energy assuming the current efficiency of the titanium cell approached that obtainable in magnesium or sodium electrolytic cell. Treatment of sponge by vacuum distillation at elevated temperatures certainly is more energy-consuming than a leaching method conducted at moderate temperatures.

4. Environmental Aspects

The actual reduction process, if operating properly, presents no substantial threat to the environment, but greater problems will be encountered in the production of titanium tetrachloride and recirculation of chlorine. Of comparable importance is the question of treatment of the sponge. If magnesium is used as the reducing agent and practically all of the magnesium chloride is recovered by tapping and subsequent distillation, the magnesium chloride can be returned to electrolytic cells for recycling

TABLE IV. Energy Requirements for the Production of Titanium Metal (Ingots) from Several Ores (Bravard et al., 1972).

(Basis: 1 ton Ti)

Gibbs Free Energy Change = 2885 kwh; Sales Price = $3200

Raw Material / Occurrence	Rutile (98% TiO_2) Beach Sands (24% TiO_2) (kwh)	Ilmenite Slag (90% TiO_2) Beach Sands (1.4% TiO_2) (kwh)	Ilmenite Slag (90% TiO_2) Rocks (20% TiO_2) (kwh)	Ilmenite Slag (90% TiO_2) Ferruginous Rocks (35% TiO_2) (kwh)	Ilmenite Slag (90% TiO_2) High Alumina Clay (~5% TiO_2) (kwh)	Ilmenite Slag (90% TiO_2) Soil (0.2% TiO_2) (kwh)
1. Mining and Beneficiation						
Drilling, Dredging, Blasting, and Stripping	56(E)	409	20(E)	15(E)	155(E)	3,680(E)
Crushing and Grinding	60(E)	119(E)	125(E)	80(E)	220(E)	5,300(E)
Gravity Concentration (Including Flotation and Drying)	19(E)	190(E)	25(E)	—	200(E)	1,720(E)
Magnetic Concentration	16(E)	143(E)	15(E)	—	55(E)	1,300(E)
High Intensity Electrostatic and/or Magnetic Separation	40(E)	595(E)	34(E)	—	190(E)	4,500(E)
Roasting	—	—	—	—	2,100	2,500
Miscellaneous (Tailings Disposal, Pumping, etc.)	40(E)	442(E)	27(E)	—	270(E)	4,300(E)
Smelting of Slag (90% TiO_2)	—	5,194(E)	5,400(E)	6,900(E)	6,500(E)	6,500(E)
Total	230(E)	7,092(E)	5,646(E)	6,995(E)	7,590(E) + 2,100	27,300(E) + 2,500
2. Processes						
Chlorination	600(E)	1,020(E)	1,020(E)	1,020(E)	1,020(E)	1,020(E)
$TiCl_4$ Purification	2,000(E)	2,200(E)	2,200(E)	2,200(E)	2,200(E)	2,200(E)
Mg Reduction Reactors	9,200	9,310	9,310	9,310	9,310	9,310
Fuel for Dry Room	11,500	11,500	11,500	11,500	11,500	11,500
Ti Sponge Purification	5,000(E)	6,500(E)	6,500(E)	6,500(E)	6,500(E)	6,500(E)
Electrolysis of $MgCl_2$	16,500(E)	16,500(E)	16,500(E)	16,500(E)	16,500(E)	16,500(E)
Equivalent of Materials Consumed (Mg, Cl_2, and C)	3,500(E) + 19,100	5,250(E) + 19,090	5,250(E) + 19,090	5,250(E) + 19,090	5,250(E) + 19,090	5,250(E) + 19,090
Consumable Electrode Furnace	5,500(E)	5,500(E)	5,500(E)	5,500(E)	5,500(E)	5,500(E)
Miscellaneous (Heating, Inert Gases)	3,000	3,000	3,000	3,000	3,000	3,000
Total	33,100(E) + 42,790	36,970(E) + 42,900	36,970(E) + 42,900	36,970(E) + 42,900	36,970(E) + 42,900	36,970(E) + 42,900
3. Totals for (1) and (2)	33,330(E) + 42,790	44,062(E) + 42,900	42,616(E) + 42,900	43,965(E) + 42,400	44,560(E) + 45,000	64,270(E) + 45,400
Equivalent Coal Energy	126,115[154,779]	153,055[190,948]	149,440[186,090]	152,813[190,622]	156,400[194,722]	206,075[261,347]

(E) = electrical energy

into magnesium metal (the reducing agent) and the chlorine can be returned to the tetrachloride plant. However, if leaching techniques are used either for residual magnesium chloride or for sodium chloride removal and the leach solutions are not used in regeneration processes for recycle, the disposal of the salt-bearing solutions must be considered an environmental and an economic problem.

B. The Hunter Process

The Hunter process uses sodium for the reduction reaction:

$$TiCl_4 + 4Na \rightarrow Ti + 4NaCl. \tag{2}$$
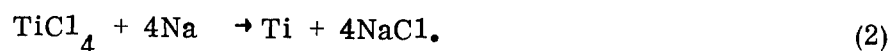
As in the Kroll (magnesium) process, the reaction is highly exothermic (-270 kcal/mole) at 900°C. Again the reaction is favored strongly by having free energy of reaction of -143 kcal/mole at 900°C. If the reaction is completed at high temperatures, back reactions do not occur during the cooling period.

Originally, the Hunter process was performed in a single step like the Kroll process and involved reacting 4 moles of Na with $TiCl_4$ as was done by Imperial Chemical and others. Today, however, a two-stage process is considered the best.

1. Present Status

The extensive work of the U.S. Bureau of Mines indicates that the process occurs in a stepwise fashion (Henrie and Baker, 1959).

> From theoretical and experimental evidence presented in this report, it can be concluded that sodium reduction of titanium tetrachloride occurs by stepwise reactions. The overall reaction can in theory and practice be broken down into two main stages. The first stage consists of a reduction of titanium chloride to titanium dichloride and trichloride in the free volume of the reactor in which local temperatures of 800° to 1000 C are obtained. These products are condensed into a fused chloride bath, with the by-product sodium chloride.

The second stage of the reaction consists of the reaction of the titanium subchlorides in the salt bath (master mix) with free sodium which is dissolved in sodium chloride. Indications are that this reaction is of a primary electrolytic* reaction between two separate phases.

Using the two-step process, large crystals of from 140 to 150 mm in length have been made in the laboratory (Ustinov, 1968). Similarly, by controlling the first and especially the second step, large crystals with very low (50-70) Brinell hardness numbers (BHN) can be obtained (Homme and Wong, 1966).

The two-stage reduction process is shown schematically in Figure 3. First, pure titanium tetrachloride ($TiCl_4$) is introduced into a continous reactor at 232°C where it combines with metallic sodium to form titanium dichloride and sodium chloride. The reaction vessel is kept under a positive pressure of argon. The titanium dichloride and salt product, which is molten and free flowing, is discharged into a sintering pot.

The sinter pot is charged with more sodium and then backfilled with argon after degassing. The second and final part of the reaction occurs here as the incompletely reduced titanium dichloride and sodium react in the sinter pot to yield a complete stoichiometric reduction of the subhalide to metal.

The second reaction is carried out at a controlled vessel temperature below 1038°C. The sponge-forming operation is not strictly crystallization, although some crystals form. As the titanium is won, it collects and agglomerates as fine particles that finally form sponge. The titanium filaments of the sponge are round in cross-section and have smooth surfaces. As the sponge mass forms in the pot, it squeezes molten salt from

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* Oxidation-reduction reaction.
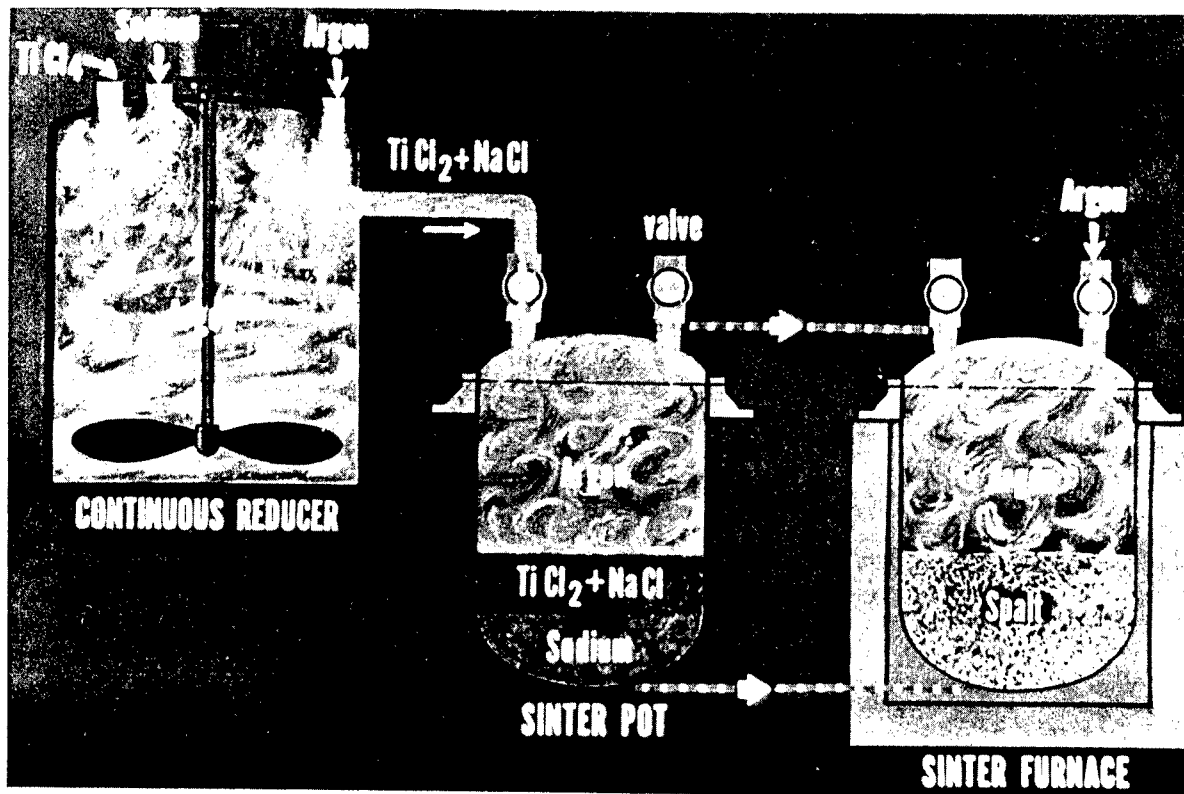
FIGURE 3. Schematic diagram of the two-stage sodium reduction process (Kessler, 1973).

the enveloping fiber network. After cooling, the sponge column is surrounded by and covered with sodium chloride.

The protective layer of salt and the mixture of sponge titanium and sodium chloride (spalt) are chipped from the pot by a remote-controlled pneumatic hammer. The spalt is crushed to 3/8-inch mesh, transported to a continous dilute acid leacher, washed with clean water, and then dried in a continuous vacuum drying unit. A typical lot of sponge may weigh 1,200 pounds after leaching.

Because water-leached titanium sponge has a higher residual salt content than vacuum-distilled sponge, RMI melting furnaces are equipped with filters and vacuum pumps. However, the cost of the filters and added vacuum equipment is insignificant when compared to the cost of vacuum distillation equipment and its operation. The added cost to melt water-leached sponge amounts to from $0.02 to $0.04 per pound, whereas the cost of vacuum distillation equipment and its operation would add as much as $0.10 to $0.20 to the production cost of each pound of titanium.

In this country, RMI in Ashtabula, Ohio, has a capacity of 5,000 tons per year (Kessler, 1973) and produces titanium by a sodium reduction process. The first stage is a continuous process, and work has been in progress to make the second stage continuous as well.

Significantly, the newest Japanese titanium sponge producer, the New Metal Products Co., uses the sodium reduction process and water leaching to reduce the residual salt content of the sponge. The titanium sponge from this new Japanese plant is identical, by all physical and chemical tests, to that of titanium sponge produced by RMI.

The major advantages of the sodium reduction process are that it is controllable due to the two-step reaction and the product can be very fine sponge or large crystals. The first stage of reduction to $TiCl_2$ can be carried out continuously by feeding $TiCl_4$ and liquid Na to a stirred reactor that discharges the $TiCl_2$-NaCl as a free-flowing product (Kessler, 1973). In the second step, which possibly can be made continuous, the remaining Na is added and reduction to metal is achieved. Other benefits include the control of metal crystal size and possibly minimizing chloride entrapment.

2. Improvements

Du Pont, whose commercial production was by the Kroll process, performed laboratory, pilot, and semi-works operations using the Hunter process (Eaton et al., June 1973; Eaton, July 1973).

Its conclusions were:

a. Sodium, used as a reductant followed by aqueous leaching, is a less expensive way to produce high-purity titanium sponge than magnesium reduction

b. Leached sodium-produced sponge presents fewer problems in melting than leached magnesium sponge

c. Sodium-produced titanium is pulverized readily to a powder suitable for powder metallurgy, obviating breaking up the sponge and melting (however, du Pont was unable to eliminate the last remnants of chlorine)

d. Small moving batches in a continuous stepwise reduction system may be an economic production method for titanium metal

RMI has done extensive research to develop a fully continuous sodium reduction process (Morse et al., 1972). Since the first stage of the RMI production process already is continuous, its goal is to develop a continuous

second stage reduction method to produce pure metal or ingot directly. A cost analysis of this process indicated significant savings over the current two-stage reduction process. RMI believes that its continuous sodium reduction process can produce titanium metal at a lower cost than any of the currently developed electrolytic processes that appear to offer only a slight economic advantage over the presently used two-stage sodium reduction process.

3. Economics

Detailed economic data for the Hunter process were not made available. Both the Kroll and Hunter processes are used commercially, indicating that neither process offers a clear economic advantage.

4. Environmental Aspects

Environmental problems are similar to those experienced in the Kroll (Mg) process. Sodium chloride leach liquors must be disposed of.

C. Electrolytic Process

In the electrolytic process for winning titanium metal, titanium tetra-chloride is decomposed in a fused salt cell. Titanium is deposited on the cathode and chlorine is liberated at the anode. The significant advantage of this process over other manufacturing methods is that it is a single-stage reduction process in which by-product chlorine is directly available for preparation of $TiCl_4$ feed. In Kroll-type processes, chlorine as well as magnesium or sodium must be generated for recycle by a additional electrolysis step.

1. Present Status

For about six years, Titanium Metals Corp. of America (TMCA) has been in semi-commercial production with this type of process using five cells, each capable of producing 190 pounds of metal per day (Minkler, 1973). A flowsheet of the process is shown in Figure 4. Purified $TiCl_4$ is fed to the

FIGURE 4. Electrolytic titanium process flow diagram (Minkler, 1973).
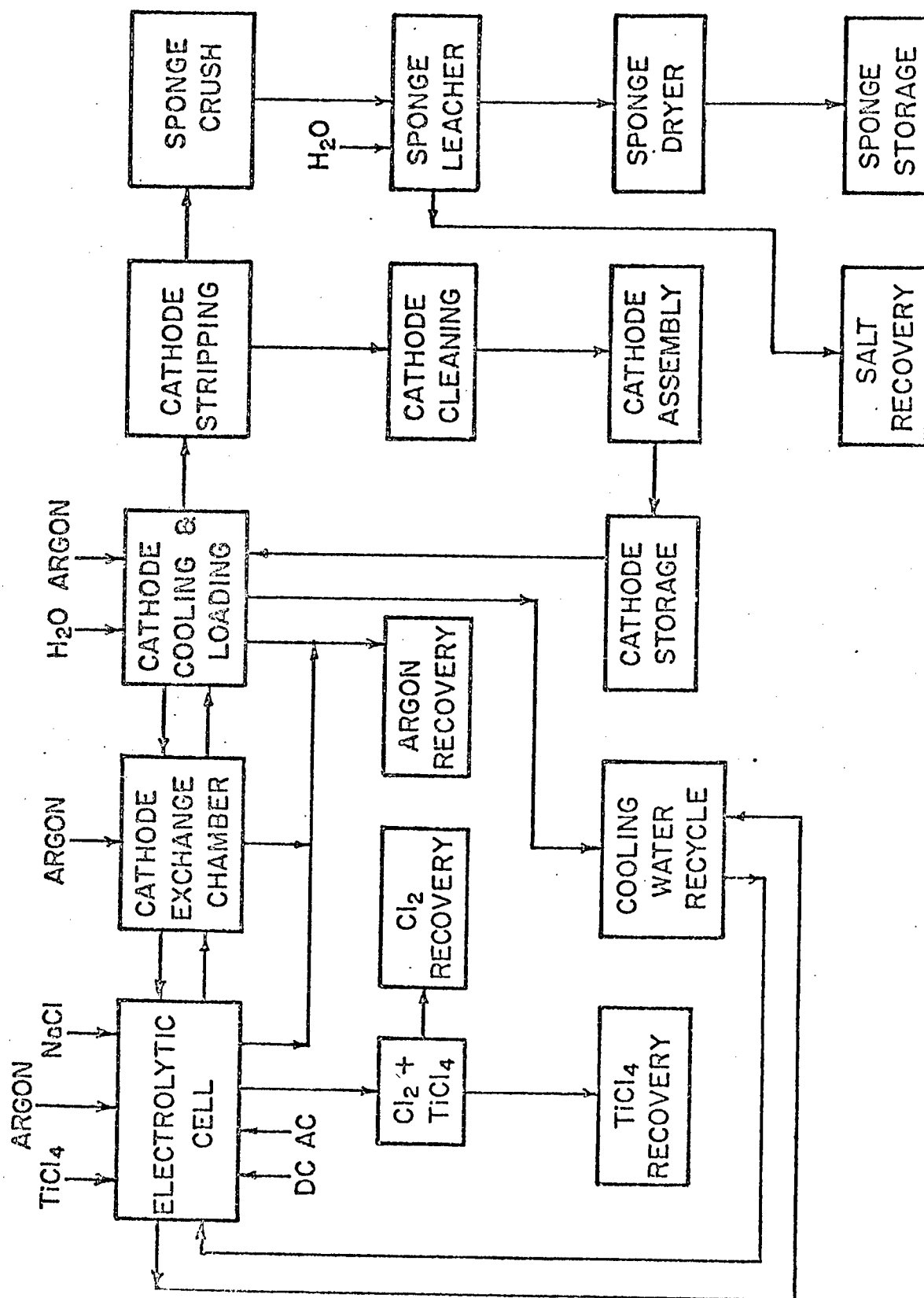
FIGURE 5. Experimental electrolytic cell assembly (Minkler, 1973).
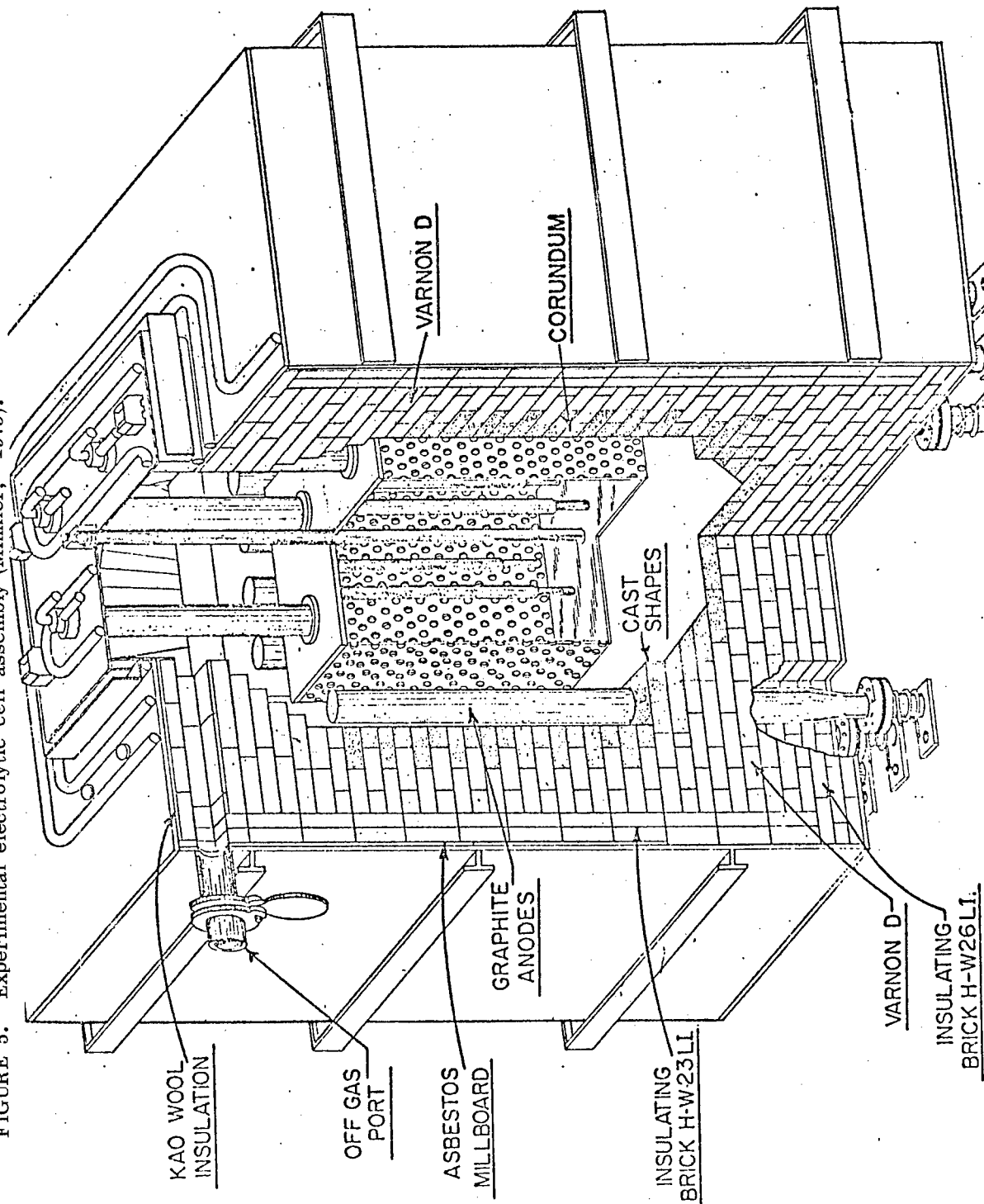
interior of a perforated metal basket-type cathode that is surrounded by an array of graphite anodes housed in a refractory-lined, gas-tight cell (Figure 5). The electrolyte may be various alkali or alkaline earth chlorides.

Titanium metal deposits on the basket cathode wall as discreet crystals and forms a porous structure dividing the electrolyte into catholyte and anolyte portions, thus playing the role of a diaphragm. Process details have not been revealed, but related publications (Opie, 1960) and patent literature (Synder, 1966) indicate a cathode current density in the range of 2 to 3 amp/in^2 and an overall current efficiency around 60 percent. Operating temperature is contigent upon the electrolyte used; for sodium chloride, 850°C is indicated.

The cathode containing about 800 pounds of deposited metal and entrained electrolyte is discharged through an inert gas cooling chamber (Priscu, 1968). The metal is recovered by removing the electrolyte in a dilute acid leach. Overall metal quality is 100 BHN or less. Since the product is in the form of discrete crystals, quality segregations can be made by screen fractionation. Selected grades (TMCA) of EL-90 (90 BHN) and EL-75 (75 BHN) have been established.

The high-purity titanium obtainable by a electrolysis offers advantages in final product properties and in the potential for new alloy development by virtue of low iron and interstitial contents (Minkler, 1973). The product is reported to be adaptable to ingot melting operations designed for distilled sponge.

2. Economics

The process has the potential for low labor costs but capital costs are high. Both considerations become more favorable with increasing scale of production. The minimum production capacity for meaningful costs reduction would be 5,000 tons per year (Minkler, 1973). In addition, larger

sized electrolytic cells, contingent upon further development work, would be required. At this scale of production using cells with a capacity of 400 pounds or more of titanium per day, the estimated selling price of sponge could be from 10 to 15 percent less than that made by the Kroll process in 1,900-pound batch reactors.

3. Environmental Aspects

Environmental problems directly related to electrolytic reduction are not serious. In this respect, the cell is operated essentially as a closed system. The cell must be gas-tight in the interest of metal quality, since the inert gas used for the protective atmosphere, the chlorine evolved at the anode, and the salt entrained in the cathode deposit can be recovered for recycle. The major waste disposal problems reside in the tetrachloride manufacture and are common to all the commercial processes.

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IV. ALTERNATIVE ROUTES – PRESENT AND PAST STUDIES

In addition to the extensive research and development work performed in perfecting the Kroll, Hunter, and electrolytic processes, effort has continued to develop other routes to titanium metal production. This work was particularly active in the early and mid–1950s and again in the late 1960s. As always, the driving force was to find either cheaper routes to the metal or competitive routes that were not covered by patents. This latter aspect led researchers to examine all conceivable chemistries that might lead to the desired product, including high–temperature processes and the use of reducing elements other than magnesium and sodium. Studies also were undertaken to take advantage of the multiple valence states of titanium and to find other electrolytic solvent systems.

These approaches can be divided into three categories: those non–electrolytic routes starting with the titanium halides, implying initial halogenation of ilmenite or rutile; those involving no halogenation; and the electrolytic processes.

A. Halide Processes

The halide processes have been studied to a much greater extent than those involving nonhalide forms of titanium compounds because chlorinating the starting material creates a product of much greater activity than the oxides themselves. Therefore, a wider variety of chemical steps may be considered for alternative routes.

1. Gaseous Reduction (Including Plasma)

The potential gaseous reduction agents are hydrogen, carbon monoxide, and hydrocarbon gases (such as methane). Carbon monoxide and methane are not satisfactory reductants for titanium tetrachloride because of

the presence of carbon, which itself leads to the formation of titanium carbide (Riter, 1973), and very little work has been reported with either agent. A study of the reduction of titanium tetrachloride using hydrogen has been made, and extremely high temperatures are required for this reaction (Kelley and Mah, 1959).

The thermodynamics of titanium production by chlorination have been reviewed rather exhaustively (Babich and Kurganov, 1968). In comparing thermal dissociation, hydrogen reduction, and disproportionation, hydrogen reduction was considered thermodynamically possible at elevated temperatures and only at high hydrogen ratios. Figure 6 is a graphic presentation of thermodynamic equilibria in the Ti-Cl-H system at various temperatures (Riter, 1973). Similar calculations that allow for the ionization equilibria differ only in an increasing fraction of singly ionized titanium atoms and electrons that appear with increasing temperature. The reduction process undoubtedly occurs stepwise through the intermediate subhalides, and the production of metal by hydrogen reduction would require selective condensation.

a. State of the Art

An arc torch has been used to generate the desired high temperature and to produce atomic hydrogen for reducing titanium tetrachloride (Casey and Berhman, 1964). Although the equipment is described in some detail, there is no indication that elemental titanium was ever produced in the system. The temperatures should be in excess of 3500°C for the arc and about 3000°C for the condenser.

On the other hand, experiments are described in which titanium tetrachloride gas and hydrogen were fed through the nozzel of a tungsten electrode that discharges to another electrode (Ishizuka, 1958). Powdery crystals were found that, when heated in vacuum, produced 99.4 percent
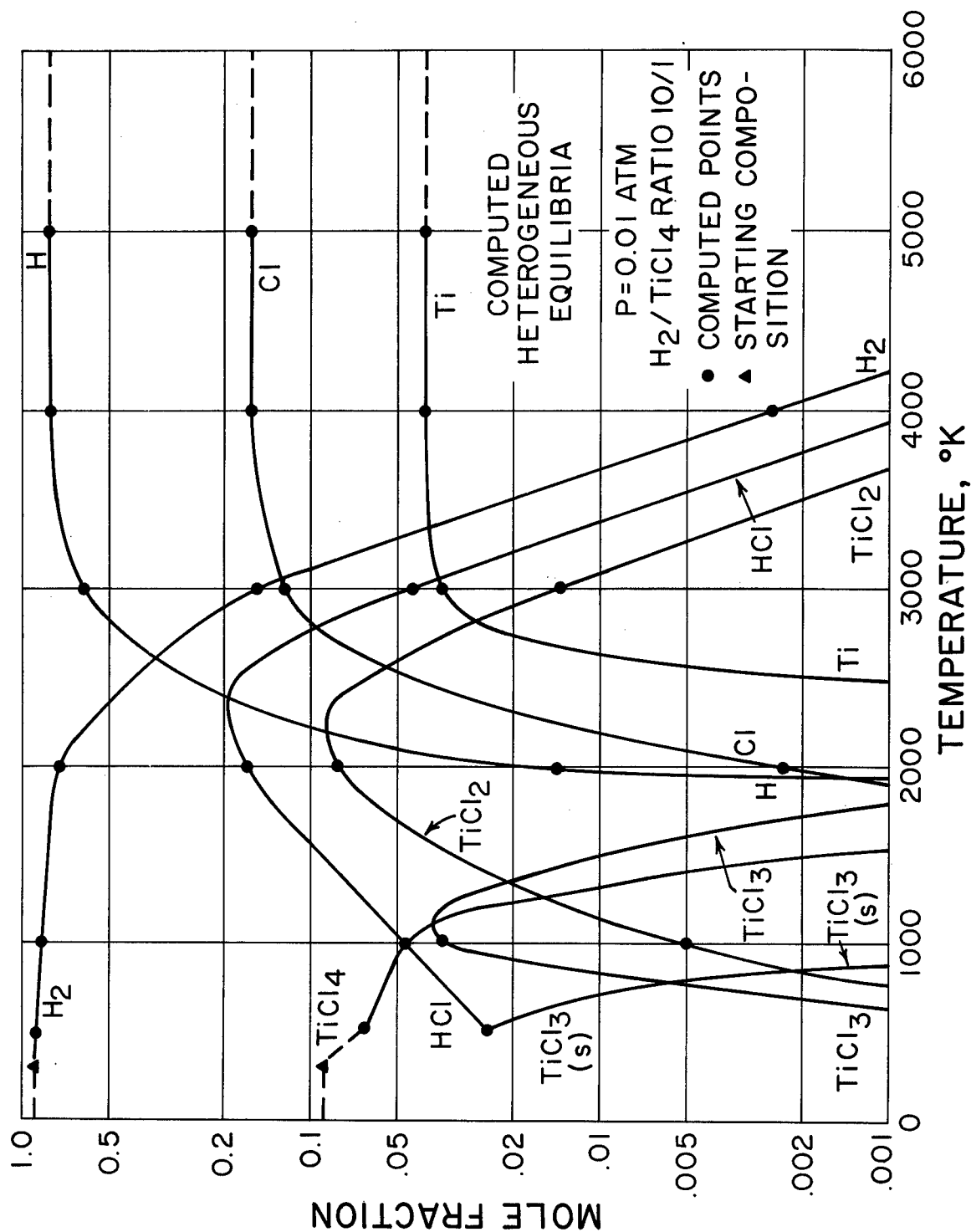
FIGURE 6. Thermodynamic equilibria for the Ti-Cl-H system (Riter, 1973).

titanium. These may have been titanium subhalide crystals that dispropor-
tionated. Similarly, titanium halides were blown into a plasma flame,
accompanied by hydrogen, and the reduced metal was found to have high
purity (Wake, 1963). Figure 7 is a conceptual flow sheet for this process,
which has been reported to make small quantities of titanium (Thorpe, 1971);
however, subsequent correspondence has indicated that in accordance with
recent thermodynamic calculations (Riter, 1973), the product was titanium
carbide (Wilks, 1973). Presumably, the source of the carbon was the
electrode.

The use of a high frequency, or induction, plasmatron has been
proposed for producing atomic hydrogen to react with the titanium tetrachlo-
ride (Mil'ko et al., 1967). A 10-to-40-kilowatt power level operating at a
frequency of 5 to 25 megacycles was proposed but apparently the concept was
not reduced to practice.

The use of an arc plasma jet to reduce halides to titanium with
a reducing agent, such as hydrogen, has been described (Little and Wentzell,
1967). The technique of feeding both the halide and the reductant into the
plasma jet torch operated at about 2000°C has been outlined. Reportedly a
"pure titanium" ingot was produced using sodium as a reductant with an 80
percent yield at atmospheric pressure and a 90 percent yield at 7 atmospheres
pressure. However, no experimental evidence of the use of hydrogen for this
purpose is provided.

An argon-hydrogen plasma to reduce titanium tetrachloride has
been suggested (Krapukhin and Korolev, 1968). This technique reportedly
will produce a maximum yield of 42 percent metal as pyrophoric, finely dis-
persed powder but it has not been reduced to practice.

SCHEMATIC – PROPOSED PLASMA PROCESS TITANIUM FLOW SHEET
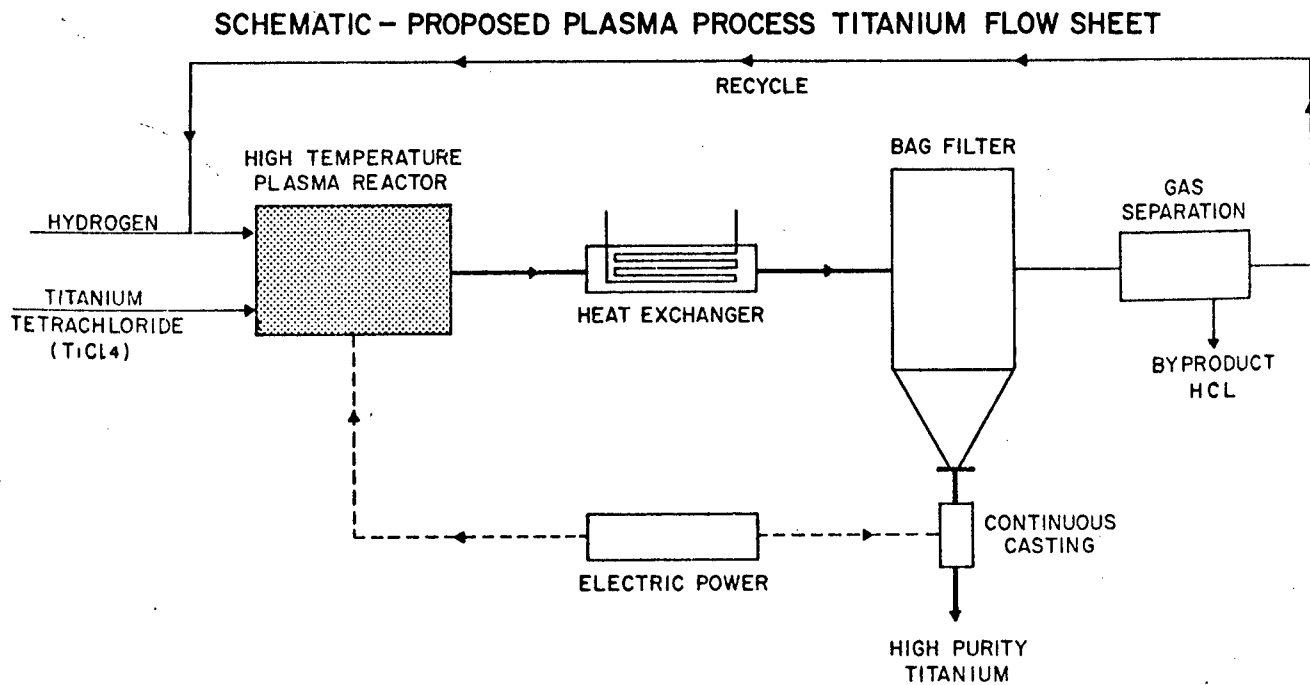
FIGURE 7. Schematic: Proposed plasma process titanium flow sheet
(Thorpe, 1971).

b. Potential Economics

As indicated above, little experimental work has been performed on the hydrogen reduction of titanium tetrachloride to form titanium metal, none of it provided engineering data, and thermodynamic considerations indicate high temperatures and excess hydrogen are required. Both of these factors bear an economic penalty.

In general, temperatures above $3000\,^{\circ}C$ are generated in a limited number of ways, two of them being plasma arc and induction plasma torches. These electrical sources are relatively expensive.

Two additional problems with high temperature sources may be corrosion and waste-heat recovery. In a reaction such as suggested here, one of the products is hydrogen chloride whose corrosiveness makes it difficult to use a plasma jet with parts such as the tungsten, copper or graphite electrodes and the steel case. This problem is not as severe in induction plasma generators where the energy is coupled directly into the gas stream by high frequency excitation and the gases carried through a ceramic or glass tube with the induction coil exterior to the reactor wall.

Part of the heat energy generated by the electrical discharge in an arc plasma jet is lost to the water that cools the materials of construction for the electrode and torch body in order to pervent their failure. Heat loss to the water cannot be recovered easily. This problem is present only partially with the induction plasma, which, on the other hand, does not have as good an energy coupling with the gas stream as a plasma arc.

Another thermal loss involves the cooling of the reacted gases to permit the condensation of the titanium metal and when the temperature is sufficiently low, condensation and removal of the hydrogen chloride.

Possibly, the gases fed to the reactors could be preheated by heat exchange, but this does not seem workable. In any event, most of the enthalpy in the reaction gas stream is not recoverable for practical purposes. These factors generally indicate unacceptable power costs per unit of titanium formed; therefore no attempt has been made to carry these hydrogen reduction processes into engineering development.

c. Environmental Aspects

As with all halide processes, there would be problems with losses of titanium tetrachloride and hydrogen chloride to the environment. If the hydrogen chloride is neutralized by lime, a waste disposal problem still exists.

2. Disproportionation

There are only two disproportionation reactions of potential interest, those involving titanium trichloride and dichloride. The latter compounds can be formed by the reaction of titanium tetrachloride with titanium, although the reaction is of no interest in the present context since a form of the product is required as a starting material. However, the titanium subhalides also could be formed from titanium tetrachloride by using hydrogen, and this is considerably simpler thermodynamically and temperature-wise than hydrogen reduction all the way to the metal itself.

Although the tetraiodide process basically is a decomposition reaction, it is covered here under disproportionation processes.

a. State of the Art

A process involving the reduction of titanium tetrachloride with hydrogen at 727 $^\circ$C to achieve titanium trichloride has been described (Ferraro, 1959):

$$TiCl_4 + \tfrac{1}{2}H_2 \rightarrow TiCl_3 + HCl, \qquad (3)$$

$$TiCl_3 \rightarrow \tfrac{1}{2}TiCl_4 + \tfrac{1}{2}TiCl_2, \qquad (4)$$

$$\tfrac{1}{2}TiCl_2 \rightarrow \tfrac{1}{4}TiCl_4 + \tfrac{1}{4}Ti. \qquad (5)$$
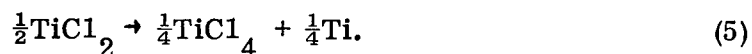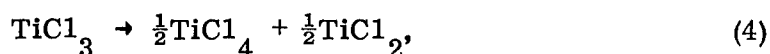
Although the temperature requirements are less stringent, the process has an excessive number of separation and reaction steps and has not been developed past the laboratory stage.

The first ductile titanium was prepared by decomposing titanium tetraiodide on a hot filament (van Arkle and Deboer, 1925):

$$TiI_4 \quad Ti + 2I_2. \qquad (6)$$

A basic limitation to this process is the high equipment cost that results because, the titanium deposit grows on the filament, the electrical resistance decreases, requiring higher amperage at a lower voltate to maintain the required temperature, 927 to 1227 $^{\circ}$C. Attempts to run at lower temperatures result in lower iodine recycle efficiency. Further, most of the apparatus of the iodine process must be constructed from corrosion-resistant materials because the free iodine attacks many substances and their iodides become a source of contamination to the titanium deposits. In fact, the filament technique has been used in a glass apparatus to make high-purity titanium metal of 60 BHN (Campbell et al., 1948).

The rate of titanium tetraiodide decomposition has been shown to be independent of filament surface area but directly proportional to vapor concentration (Bowling, 1963). This decomposition reaction is probably a first order gas phase reaction occurring in a hot zone around the filament rather than a heterogeneous reaction occurring at the filament surface. Thus, the majority of the titanium atoms from the decomposition in this hot

zone are not collected by the filament but are dissipated throughout the vapor. They then may recombine with the iodine liberated by the decomposition or react with titanium tetraiodide to form lower iodides,

An attempt was made to solve this problem by film-boiling the titanium tetraiodide liquid on a heated filament rather than operating the reaction totally in the gas phase (Peterson and Bromley, 1956). The deposition rate was higher and the energy requirements smaller than in the van Arkle process, but it was concluded that many problems must be solved before the process is commercially feasible.

A number of investigators have tried to bypass the use of the electrical filament for the reasons mentioned above. In one case, titanium tetraiodide was fed through a hollow electrode (Suva and Tietz, 1959), but although the patent describes the details of the equipment and process, there is no indication of actual metal being produced. An electric arc also has been used to decompose the tetraiodide in the vapor phase and then nucleation points were provided for the condensing of the titanium by introducing finely divided titanium metal (Weir, 1961); product quality, however, was not described. A similar approach was suggested in which the tetraiodide is reacted in a dissociation furnace having a relatively cool wall at which the halide decomposes while metallic titanium particles are introduced and inductively heated to about 1200° C to provide a surface upon which the titanium metal could deposit (Dunn, 1958).

The production of titanium carbide has been proposed as the starting point for the manufacture of tetraiodide (Loonam, 1955). Nitrides and oxycarbides also are suitable starting materials.

b. Potential Economics

Problems with the titanium chloride disproportionation, from an economic viewpoint, are the excessive number of reaction and separation steps and the need to recycle the hydrogen chloride.

The three steps in the tetraiodide process would be: (1) the formation of a titanium carbide, or oxycarbide, by the carbon reduction of titanium dioxide; (2) the reaction of this material with iodine to form the tetraiodide; and (3) the decomposition step to metal and iodine, recycling the iodine. The production of the tetraiodide presents the same process and economic problems as the preparation of the tetrachloride. An additional economic barrier to this process would be the iodine, since 10.6 pounds are required for each pound of titanium. Iodine at a cost of $2.25 per pound would be equivalent to an extra $0.24 per pound on the cost of titanium for each 1 percent of iodine lost during the cycle. In addition, this material, like any other halogen, would be a pollution problem so that losses also would lead to pollution control costs.

c. Environmental Aspects

The environmental considerations regarding disproportionation reactions are the same as those for processes involving halogens.

3. Metallothermic Reduction

The commercial use of the Kroll and Hunter processes has naturally lead other investigators to examine the possibilities of further modification or of using other active metals to reduce titanium tetrachloride. Some of these results are summarized below.

a. State of the Art

A new single-step Hunter-type process that produces solid titanium by the reduction of titanium chloride with sodium has been described (Hurd, 1972). Sodium is introduced into a large steel vessel and a stoichiometric amount of titanium chloride is added. Then, the top of the large steel vessel is welded to the container. The closed container now is heated slowly without shaking to 180° C, which is above the melting point of sodium. Next, the container is removed from the heating mantle and shaken very strongly vertically. The shaking mixes the liquid sodium and liquid $TiCl_4$ layers and starts the reaction. The bottom part of the vessel becomes red-hot. After the reaction is complete, 95 percent of the titanium is recovered, half of which comes out as a big lump and the other half as small nodules.

Aluminum reduction of $TiCl_4$ was stated to occur at 200° C, with the subsequent separation of $AlCl_3$ from the resultant titanium subchlorides not difficult because of the wide differences in their temperatures of sublimation (Henrie, 1965). Experience at de Pont has provided additional information on aluminum reduction of $TiCl_4$ (Eaton, 1973). When the vapor was passed over Al metal slightly above its melting point, a very rapid reaction occurred forming the solid compound Al_3Ti (37 weight percent Ti) along with by-product $AlCl_3$. An alloy containing 85 weight percent Ti was obtained by the protracted flow of $TiCl_4$ over the Al_3Ti as the temperature was increased gradually to 1285° C. In this operation, some Ti is also lost as lower chlorides that deposit outside the hot zone. Alternatively, the Al_3Ti may be heated in a fused salt consisting of $TiCl_2$, $TiCl_3$, and NaCl in order to remove Al. This technique was used to increase the Ti content of the alloy above 90 weight percent but du Pont concluded that this process was not practical and dropped the study. As described in U. S. Patent No. 3,252,823,

it is possible to devise a two-step process in which, first, $TiCl_4$ is reduced to lower chlorides by Al in a fluidized bed and, second, these lower chlorides may be dissolved in NaCl and further reduced to Ti metal by sodium. Both steps were demonstrated and probably they could be carried out on a commercial scale. However, it was difficult to see any outstanding cost or purity advantage versus one-step sodium or magnesium reduction (Eaton, 1973).

The salient features of the uses of other alkali or alkaline earth metals for reduction of $TiCl_4$ have been summarized (Henrie, 1965). The use of these metals depends on their physical properties, cost, and purity as compared to sodium and magnesium. Lithium has a lower vapor pressure than sodium at a given temperature and, hence, would not vaporize from the reaction zone as readily. Lithium chloride also melts at a lower temperature than does sodium chloride, allowing the reduction reactions to take place at lower temperatures. Calcium reduction has these same advantages. However, since lithium and calcium metal production technologies currently are not as advanced as those of sodium and magnesium, it is doubtful that the former metals would be available at equivalent cost and purity.

b. Potential Economics

None of the alkali or alkaline earth metals can compete with sodium and magnesium in the cost-purity relationship, although the two-step process using aluminum was stated to be as costly as the sodium reduction process in producing pure titanium (Eaton, 1973).

c. Environmental Aspects

Environmental impact is considered roughly comparable to that of the Kroll and Hunter processes in the primary effects.

B. Non-Halide Processes

These processes involve the use of rutile or ilmenite directly or their conversion to various non-halide compounds such as titanium carbide, nitride, etc.

1. Gaseous Reduction (Including Plasma)

The only plasma process involving the production of metallic titanium is the reduction of rutile by hydrogen.

a. State of the Art

The introduction of rutile into a plasma chamber where it would be melted into finely divided liquid droplets which then would be contacted in countercurrent flow with a hydrogen plasma that reduces the liquid oxide to titanium with resultant formation of water vapor has been suggested (McLaughlin, 1969).

$$TiO_2 + 2H_2 \rightleftharpoons Ti + 2H_2O \tag{7}$$
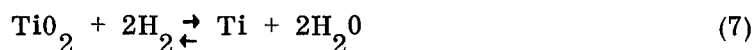
Then, the liquid titanium would be recovered as finely divided droplets. The process is expected to be conducted around $3000\,^{\circ}C$ so that the reaction would go to completion. In actual experiments, a Giannini P-140 plasma jet was utilized with a primary working fluid of helium and hydrogen and with the rutile in the form of paint pigment. The product was claimed to contain 99.8 percent titanium and 0.1 percent aluminum, but the recovery was not given.

b. Potential Economics

No attempt has been made to commercialize this process, probably for the reasons mentioned in Section IV-Alb, unacceptable power costs.

c. Environmental Aspects

In the case of the hydrogen reduction of rutile, no environmental problems are envisioned since the only products would be titanium metal and water.

2. Metallothermic Reduction

In the past,calcium, magnesium, aluminum, carbon and calcium carbide have been considered for the direct reduction of titanium dioxide because of their availability and reducing potential (Henrie, 1965).

a. State of the Art

The possibility of using alkaline earth metals as reducing agents was studied by many and summarized by the Bureau of Mines (Mah et al., 1957). Work showed that calcium has a reducing potential sufficient to obtain a product containing 0.04 to 0.07 weight percent oxygen at 1000°C. Magnesium metal will reduce the oxygen in titanium to a theoretical value of 1 to 2 weight percent. Aluminum forms stable alloys with titanium, but an excess of Al is required (Kubaschewski and Dench, 1955); e.g., if the reduced product contains approximately 0.1 weight percent oxygen, it also has 56 to 63 weight percent aluminum weight, while products with only 5 weight percent aluminum have over 11 weight percent oxygen. Calcium was considered the only commercially available reducing agent with sufficient potential to reduce TiO_2 directly to titanium metal (Henrie, 1965). In the past, this process was run by the Dominion Magnesium Co., Metal Hydrides, Inc., has produced titanium powder by reduction of TiO_2 with CaH_2 (organization for European Economic cooperation, 1956), but this process led to brittle titanium products.

b. Potential Economics

No information is available but the considerations mentioned in Section IV A-3b apply.

c. Environmental Aspects

Problems, while still relatively minor, are of a different nature with metallothermic reduction than with carbothermic reduction. The handling of oxidized reductant products would present some problems, though not as serious as those concerning halide systems because of the limited solubility of the oxides produced.

3. Metallothermic Reduction with Alloy Formation

The "Henrie" diagram (see Figure 1, p. 5) was used by the Panel and an effort was made to determine if the alternative processes suggested by the diagram covered all possible routes. The Panel identified one possible variation involving titanium alloy formation that bypassed an electrorefining step in one of the routes. A patent assigned to the Ontario Research Foundation describes the process in which titanium dioxide is reduced directly by a metallic reducing agent to form titanium alloy plus a slag of the oxide of the reducing metal (Brandstatter, 1973). The alloy is then refined chemically to produce pure titanium.

a. State of the Art

The reducing metal is consumed in forming the oxide slag and the titanium alloy. This suggests removal of as much oxygen from the starting material as possible; therefore, the patent proposes either a carbon reduction to obtain a lower oxide of titanium or an electric carbon arc reduction for this purpose or even to form titanium carbide.

Suggested as the reducing metal is aluminum that forms a stable $TiAl_3$ alloy as well as a very stable aluminum oxide slag. The reaction is performed in a thermite reactor, and the alloy is transferred to a cleanup reactor where vacuum distillation removes the bulk of the unalloyed aluminum. Then, calcium metal is added to the reactor to reduce the residual oxygen content of the titanium to approximately 0.3 percent. In the next step, using the same reactor, the molten metal is subjected to chlorination to remove the unreacted calcium and aluminum from the titanium-aluminum alloy. Finally, another calcium deoxidation is performed.

The patent implies production of high-purity titanium with residual oxygen contents of about 200 parts per million.

b. Potential Economics

As mentioned earlier, a major factor in the costs of this process will be the consumption of aluminum. If $TiAl_3$ alloy and aluminum oxide are formed, then 4.33 moles of aluminum are required per mole of rutile and 3.67 moles per mole of titanium monoxide. On the average, 2.25 pounds of aluminum are consumed for the production of 1 pound of titanium. This means a materials cost of $0.64 per pound of titanium just for the aluminum alone.

As stated in the patent, the process removes any manganese present in the original TiO_2 but does not remove residual silicon, iron, or vanadium effectively. In general, natural rutile contains up to 0.6 percent iron and rutile prepared by the beneficiation of ilmenite contains even more. Accordingly, titanium quality will be affected when these impurities are present. Another economic factor is the life of the refractory in the refining vessel. The patent proposed the use of calcium oxide for containing the liquid titanium, but no real refractory for this purpose has been found yet.

c. Environmental Aspects

Metallothermic reduction presents a number of possible pollution problems. First, an aluminum oxide slag is formed in the thermite reaction and it must be stored, or possibly recycled, by reprocessing in an aluminum plant. The economic question is whether the cost of shipping will justify its return.

Gaseous leakages are possible in the chlorination refining step at the end of the process. Most likely, the aluminum chloride could be recycled by oxidation to recover the chlorine for reuse in the process and to prepare aluminum oxide for return to the aluminum plant. On the other hand, the calcium chloride probably would go from a scrubber into waste water and would constitute a water pollution problem.

4. Carbothermic Reduction

It is claimed that titanium metal may be produced on a commercial scale by reducing the finely divided TiO_2 with natural gas (Dotterweich, 1942). It is, of course, easy to write balanced equations for this and other processes, but these may be misleading as in the single-step plasma reduction of the tetrachloride to the metal with hydrogen. This process proposes using finely divided ores of Ti, as well as V, Cr, Fe, and Ni. It was conceived as a means of reducing ores in locations where coking coal is unavailable and, hence, is of little interest here.

a. State of the Art

Carbon is the cheapest material that can reduce TiO_2 effectively; therefore, many attempts have been made to obtain the metal this way. Experiments have shown that the product is a mixture of titanium, carbon, and oxygen and that its composition is influenced largely by the reduction

temperature, charge composition, and availability of carbon to the charge.

To unravel these effects, a calculational and experimental program was followed and Figure 8, a theoretical Ti-O-C composition diagram, was developed (Henrie, 1965). These calculations were checked by taking an arc furnace product (consisting primarly of titanium, oxygen and carbon) and melting it several times on a water-cooled cooper plate under a helium atmosphere in a tungsten electrode arc furnace (Henrie, 1965). The temperature of the molten specimen was 300 to 400 $^\circ$C above the melting point of titanium, or about 2127 $^\circ$C. As shown on Figure 8, chemical analysis indicated that the initial product had a composition of point 81.9 percent Ti (Point A), with the remelted product composition corresponding to Point B. The composition changed during melting parallel to the CO line and reached a value of 87.2 percent Ti.

The reduction also was performed by induction melting of the material in a graphite crucible. Excess carbon was of course available and chemical analysis showed that the composition shifted from Point A to Point C, indicating that as the oxygen was removed the carbon content increased in the melt. If oxygen had been readily available to the melt, the composition of the product would have shifted toward the right until the approximate composition Ti_2O_3 was reached. These data illustrate that it is possible to obtain products richer in titanium than the TiO-TiC tie line of the ternary, but in practice a product of 82 to 83 percent Ti is about the best to be expected by carbon reduction. In an arc furnace, where excess carbon normally would be available, the product would have a composition to the left of the carbon monoxide line.

This carbon-reduced near-homogeneous material is conceptually the starting point of the Brandstatter process discussed in Section IV-B3.
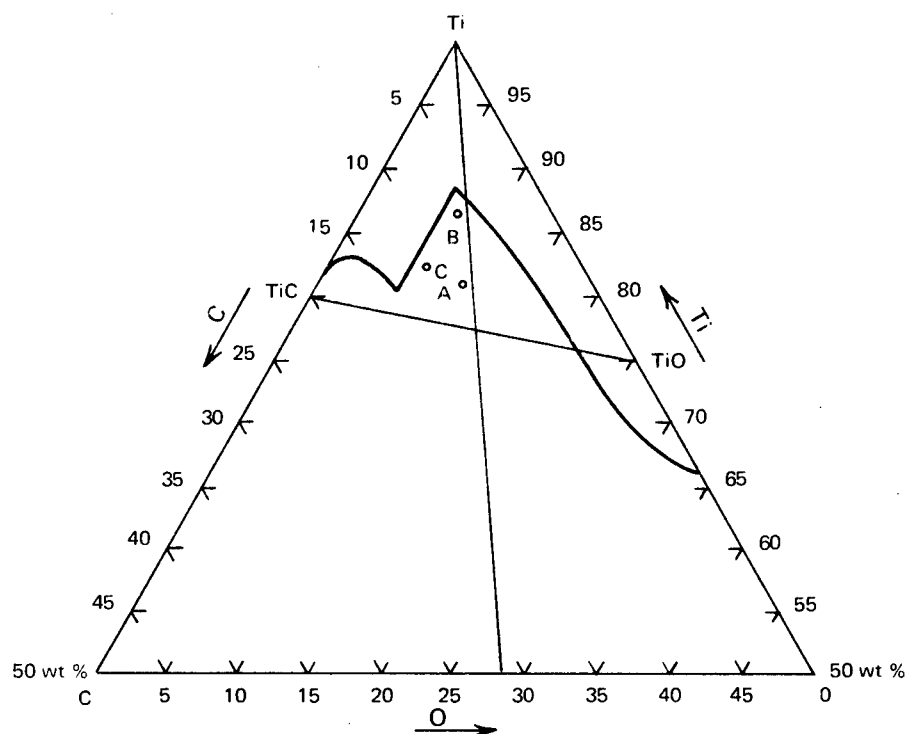
FIGURE 8.   2127°C Isothermal ternary diagram of Ti-O-C system, extent of carbon reduction of titanium oxides (Henrie, 1965).

See text for discussion of Points A, B, and C.

This route is not a feasible method for the direct reduction of titanium products.

b. Potential Economics

Carbon is, of course, cheap, but the product is not comparable to that produced in the Kroll, Hunter, or electrolysis processes.

c. Environmental Aspects

Carbon monoxide would be generated in these processes.

5. Intermediate Sulfidization

An alternate non-halide route is to convert the titanium oxide to the sulfide. This might have an advantage (Henrie, 1965) because the solubility of sulfur in titanium is less than 0.02 weight percent (Hansen, 1958) and sulfur has little effect on the mechanical properties of titanium. Titanium sulfides have been produced by the reduction of titanium oxide; however, because of their stability, strong reducing agents, such as magnesium, are required to prepare pure titanium, and titanium monosulfide would be preferred to conserve the reducing agent (Henrie, 1965). In fact, if the sulfides are not in their reduced state, they could react to form sulfides with iron and other common metallic materials used to construct reactors.

a. State of the Art

As indicated above, the process starts with rutile. However, a possible advantage of this route is that there could be a process for preparing rutile from ilmenite through a sulfide route (Hiester et al., 1974); such a process would involve the reduction-sulfidization of the iron at about $900\,^{\circ}C$ to make it more soluble. The rationale behind this approach is the chemical similarity of sulfur and oxygen and the relative stability of the oxide of

titanium (compared to its sulfide) is much greater than for the similar iron sulfide pair. Further, the greater ionic radius of the sulfur atom, compared to oxygen, should help break up the ilmenite lattice.

The obvious reactant is hydrogen sulfide. A cyclic process is possible when dilute hydrochloric acid is used to dissolve the iron sulfide and the metal chloride subsequently is decomposed in the presence of steam and air.

Sulfur dioxide also might be used as a sulfidizing gas but it requires the presence of a reducing agent. Again, a cyclic process is apparent (Hiester, 1971). If sulfur dioxide is used as the leaching agent, elemental sulfur is formed by the Claus reaction because of the reaction between the sulfide and sulfite ions. This necessitates an extra step in which the sulfur must be oxidized away from the rutile residue unless it is used in preparing the titanium sulfide.

Rutile, whether derived from ilmenite or as an original ore, now can be reduced in the presence of sulfur to form titanium sulfide. Actually, a wide variety of these compounds exists with varying stoichiometry (Abendroth and Schlechten, 1959). The preferred form would be the monosulfide or lower since its reduction would involve the use of less magnesium. The formation and reduction steps are shown below:

$$TiO_2 + S + 2C \rightarrow TiS + 2CO, \qquad (8)$$

$$TiS + Mg \rightarrow Ti + MgS. \qquad (9)$$
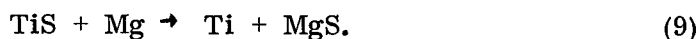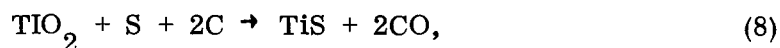
Ultimately, the magnesium must be recycled so the sulfide might be decomposed by chlorine and, then, the magnesium chloride electrolyzed to regain the magnesium and chlorine (as in the present Kroll process). These steps are shown below:

$$MgS + Cl_2 \rightarrow MgCl_2 + S, \qquad (10)$$

$$MgCl_2 \rightarrow Mg + Cl_2. \qquad (11)$$
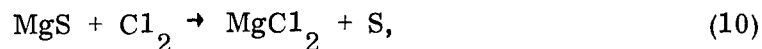
All the above reactions, except for the last, which would be driven electrically, are thermodynamically feasible.

There has been some study of these reactions. A number of methods for producing titanium sulfide were tried at the U.S. Bureau of Mines at Rolla, Missouri (Knickerbocker, et at., 1949). In these reactions, the sulfur source was pyrites; the reducing agent was coke; and both rutile and ilmenite were used as feed material. The magnesium reduction of titanium sulfide was studied at the Aachen Institute fur Inorganische Chemie and fur Electrochemie, where titanium purities as high as 99.5 percent were obtained with ductile titanium resulting (Schwartz and Koster, 1956).

The sulfide approach also was studied by a large minerals company and, although the findings have not been published, there were problems with this process (Schlechten, 1973). The New Jersey Zinc Company also studied titanium sulfide as an intermediate for the production of titanium metal (Reimert, 1973) and explored the electrolysis of titanium monosulfide in molten salt baths of the potassium and sodium sulfides. Although good solubility of feed and good electrical conductivity of the solvent was experienced, in each instance, the titanium was complexed as an anion that migrated to the anode and resulted in the deposition of compounds containing only smaller amounts of titanium.

It also has been reported that titanium monosulfide can be reduced partially by reacting with titanium carbide at $2200\,^\circ C$ to yield a product containing approximately 92 percent titanium, 3 percent sulfur, and 5 percent carbon (Wainer, 1958). This product could be electrorefined to yield ductile titanium metal.

b. Potential Economics

The sulfide route presents some major problems that could affect its economic viability. For instance, there must be a way to separate magnesium sulfide from the reduced titanium. Since it is neither water soluble nor easily volatilized, it must be hydrolyzed and dissolved in dilute acid. Next, the starting rutile must be quite pure since sulfides of the contaminating metals stay with the matte and cannot be separated as easily as with the titanium tetrachloride and, as a result, these impurities carry through to the titanium metal (Knickerbocker, et al., 1949). Finally, there is a materials of construction problem since the sulfur reactants, at the temperatures involved, easily attack metallic materials of construction for the reactor.

Titanium tetrachloride, since it can be purified, has been suggested as a starting material. The sulfides then could be produced by reaction with hydrogen sulfide, but economic benefit is apparent since the titanium tetrachloride can be reacted directly with the magnesium rather than by way of a sulfide.

c. Environmental Aspects

In view of the necessity to regenerate the magnesium chloride, a chlorine pollution hazard exists. The use of sulfides in the system presents another potenital pollution problem since these can generate fumes as toxic and perhaps even more annoying than those of chlorine. Therefore, a reaction involving a sulfur step must provide for recovery of sulfur effluents.

C. Electrolytic Processes

1. Aqueous Electrolytes

Titanium is high in the electrochemical displacement series and thus has a high deposition potential. The cathode potential required for reduction is sufficiently higher than that for release of hydrogen essentially to preclude deposition from aqueous electrolytes on theoretical grounds. Nevertheless,

repeated attempts have been made with little success. Thin coatings of titanium or of alloys of titanium with the cathode metal reportedly have been electrodeposited on cooper, nickel, or iron cathodes from alkaline solutions of sodium titanate (Kudryavtsev and Golovchanskaya, 1963); however, the hydrogen overvoltage for titanium and the titanium alloys is so low that titanium deposition ceases after the base cathode metal becomes coated.

Since titanium does not form amalgams readily, the high hydrogen overvoltage associated with this type of cathode cannot be utilized. Other liquid-metal cathodes have been considered, but none has been found with the proper characteristics.

2. Nonaqueous Liquid Electrolytes

Many attempts have been made to electrolyze solutions of titanium compounds in organic solvents resistant to electrochemical reduction (Creamer et al., 1954; Reid et al., 1957). Partial reduction of titanium tetrahalides or tri- or even di-valent forms can be accomplished in a variety of organic solutions, but complete reduction to metal has not been achieved. Precipitation or deposition of lower valent compounds due to low solubility is a problem; however, the basic limitation is reduction of the solvents before the titanium is reduced completely.

Electrolysis of titanium halides in liquid ammonia has been investigated extensively without success (Creamer et al., 1954). Low solubility in this system is a serious limitation, but, more importantly, only partially reduced complexes were deposited.

3. Fused Salt Electrolytes - Halide Feeds

By far the greatest success in electrowinning of titanium metal has been realized with the use of fused salts as the electrolyte, particularly with alkali or alkaline earth halides. The utility of these salts derives from the

fact that the deposition potential for the alkali and alkaline earth metals is higher than that of titanium and, in addition, the melts have good electrical conductivity.

The most successful developments have been in the use of titanium tetrachloride as the feed material. $TiCl_4$ is only sparingly soluble in fused alkali chloride melts but the lower chlorides, $TiCl_3$ and $TiCl_2$, are highly soluble. To avoid reoxidation of lower chlorides at the anode, which would result in low current efficiency as well as loss of $TiCl_4$ with the chlorine, it is essential for the cell to be divided into anolyte and catholyte compartments. Many attempts have been made to use porous ceramics as a diaphragm '(Leone et al., 1967). Although high-quality metal can be prepared through the use of such materials, diaphragm service life has been unsatisfactory. Generally, materials resistant to chemical attack, when simply immersed in electrolyte containing dissolved lower chlorides, rapidly deteriorate by cracking and exfoliation when subjected to electrolyzing current.

The Dow Chemical Co. has developed a porous diaphragm that has a long service life at economically practical current densities (Cobel, 1973; Turner, 1973). No details about diaphragm construction have been revealed but a 2,000 ampere cell has operated successfully. $TiCl_4$ was electrolyzed in an alkali halide bath to titanium producing an ingot hardness as low as 70 BHN. Dow and Howmet Corp. now have signed an agreement for further development and commercial scale-up of the process (American Metal Market, 1973). It is anticipated that the process will require much less capital investment than the conventional Kroll process and that a plant with a capacity as low as 1,500 tons per year would be economically viable.

Titanium Metals Corp. of America (Priscu, 1968) and New Jersey Zinc Co. (Myhren et al., 1968) have developed processes fulfilling the compartmental requirements through unique cell designs and modes of operation. The cells and their operation result in deposition of titanium metal as a porous

mass on perforated cathodes in such a manner that the combination serves as the diaphragm structure required to separate the catholyte from the anolyte. The Titanium Metals Corp. process has been used in semi-commercial production and is described in Section III.

The New Jersey Zinc Co. process was operated on a pilot-plant scale in 1958. The cell had a diameter of 72 inches and was made of nickel alloy. A cylindrical graphite anode in the center was surrounded by a perforated nickel cylinder serving as the cathode. The cell was provided with gas-tight seals and operated under an atmosphere of argon. The electrolyte was a eutectic mixture of KCl-LiCl-NaCl having a melting point of 362°C.

The maximum cathode current density during titanium deposition was 3 amp/in^2. The catholyte temperature during operation was 500°C but, near the end of a run, it was decreased to about 400°C. This was low enough to permit withdrawing the loaded cathode directly to the open atmosphere. The deposit consisted of about 900 pounds of porous titanium metal and about an equal weight of entrained electrolyte that was removed subsequently by leaching in 0.5 percent HCl. Metal particles larger than 200 mesh were separated as useful product. In good runs, this portion was equivalent to about 90 percent of the TiCl$_4$ feed and could be melted into ingots of 100 to 115 BHN.

Because of deterioration of the titanium metal market, the pilot plant operation was not completed. However, after termination of the project, an estimate was made of a commercial facility for production of 20 tons of metal per day. Cells 86 inches in diameter carrying 42,000 amperes were visualized. A 1968 update of the original estimate indicated a capital cost of $27,000,000 and a manufacturing cost of $1.10 per pound (Reimert, 1973).

Another process, based on a halide feed, was developed to a pilot scale by Horizons Titanium Corp. (Steinberg et al., 1955; Topinka et al, 1956). Here, potassium fluotitanate was electrolyzed in fused sodium chloride. Although the cell feed in this process is a fluoride, chlorine is liberated at

the anode. As a consequence, as the cell reaction proceeds, sodium chloride in the starting bath is converted to sodium fluoride and potassium fluoride also accumulates in the melt. Since K_2TiF_6 is directly soluble in the electrolyte, this process could be carried out without recourse to the diaphragm. A graphite crucible served both as the melt container and as the anode. The unit was enclosed in an outer metal shell to permit operation in a protective atmosphere of argon. A rod cathode was suspended in the center of the melt with provision for cooling the cathode deposits in an inert atmosphere during harvesting. Deposits contained about 50 percent salt that was removed by a dilute sulfuric acid leach. The yield of titanium metal was equivalent to about 80 percent of the feed and represented a current efficiency of about 50 percent. Metal quality was in the range of 110 to 160 BHN.

There was a gradual build-up of KF and NaF in the electrolyte and, eventually, it became unsatisfactory for electrolysis. The spent electrolyte was used to prepare K_2TiF_6 feed by reaction with $TiCl_4$ made using chlorine evolved from the electrolysis (Young et al., 1956).

4. Fused Salt Electrolytes – Nonhalide Feeds

Considerable research has been conducted on electrowinning titanium directly from the oxide. In the interest of economy, this is a logical potential feed material since rutile (TiO_2) is one of the major ore minerals. However, metal of commercial purity has not been prepared by direct electrolysis.

At temperatures above the melting point of titanium, metal has been deposited from TiO_2 dissolved in calcium fluoride (Hashimoto et al., 1971). However, the product was contaminated with 2 to 4 weight percent oxygen as well as with carbon from the graphite cathode. An additional electrolytic refining step is needed to achieve the purity required for ductility.

Attempts to electrolyze TiO_2 at lower temperatures, $1000^\circ C$ or less, in calcium chloride and a variety of alkali halide melts have resulted in only partial reductions to the lower oxides of titanium (Siebert and Steinberg, 1956).

However, TiO_2 can be reduced directly to titanium metal by calcium in a modified electrolytic cell (Olson, 1958). In this process, fused $CaCl_2$ is electrolyzed between an iron cathode and a graphite anode. Calcium reduced at the cathode dissolves in, or complexes with, the molten bath to as much as 15 percent in excess of stoichiometric for $CaCl_2$.

The melt from the vicinity of the cathode is circulated through a perforated basket of TiO_2 pellets suspended in the bottom of the cell. Here, the excess calcium reduces TiO_2 and calcium oxide is formed. By continued circulation of the melt, the calcium oxide in solution is directed to the vicinity of the graphite anode where normal calcium chloride is reformed by electrochemical action and oxygen is released as carbon monoxide at the expense of gradual consumption of the anode. The electrolysis and circulation are continued until the TiO_2 pellets are reduced completely to metal as evidenced by cessation of carbon monoxide evolution at the anode. Ductile titanium containing 0.1 percent or less oxygen can be formed.

Titanium also can be deposited from TiO_2 dissolved in fused calcium chloride through the formation of alloys with liquid metal cathodes. Then, an additional refining step is required to separate the titanium from the alloying metal. A unique type of cell has been developed to pursue both types of electrolysis concurrently (Slatin, 1958). A bipolar liquid metal electrode serves as the cathode for the first or electrowinning stage and as the anode for the second or refining stage. In the first stage, titanium was deposited in a molten 28 percent copper – 72 percent titanium cathode from a feed of pigment-grade titanium dioxide to a molten bath of calcium chloride and calcium fluoride. The released oxygen reacted with a consumable graphite

anode and evolved as CO and CO_2. In the second stage, the molten copper-titanium alloy served as the anode of a low-voltage refining cell. Here, the electrolyte was a molten mixture of calcium and sodium chlorides containing titanium dichloride in solution. The refined metal was relatively free of entrained salts and was recovered by washing in cold water. Products were reported to contain 99.9+ percent Ti with a hardness in the range of 40 to 60 BHN. In later electrorefining studies by the U. S. Bureau of Mines (Kleespies and Henrie, 1964), significant amounts of copper were found to transfer with the titanium in refining from fused copper-containing alloys in sodium chloride electrolyte containing lower titanium chlorides. However, the transfer of copper could be suppressed greatly when the dissolved titanium in the electrolyte was in the form of fluorides.

Titanium can be prepared by electrolysis of the monoxide in fused calcium chloride (Siebert et al., 1955). Although metal of good crystallinity is deposited, oxygen contamination is too high to permit adquate ductility.

Titanium nitride can be electrolyzed in a mixed bath of sodium chloride and potassium titanium fluoride (Siebert, 1961). Nitrogen is evolved as a gas, and titanium containing less than 0.1 percent oxygen and less than 0.05 percent nitrogen is deposited. Hardness as low as 155 BHN is reported but even this is too high for good ductility.

Titanium metal of comparable ductility has been prepared from titanium carbide by using it as a consumable anode for electrolysis in a mixed bath of sodium chloride and potassium titanium fluoride.. Impurity analyses as low as 0.05 percent carbon and 0.12 percent oxygen were realized but ductility was inadequate (Ervin et al., 1959).

Apart from the generally unsatisfactory titanium metal quality realized from monoxide, nitride, or carbide cell feeds, these materials entail an economic penalty. At the purities required for cell feeds, the costs per unit of titanium are presently higher than in the dioxide. If titanium carbide of

the required purity could be made in an electric furnace directly from mineral rutile, rather than high-purity TiO_2, the overall costs might be lowered considerably (Glasser, 1973). However, the metal obtained by fused-salt electrolysis of such feed undoubtedly would require an additional electrolytic refining treatment to obtain the purity required for good ductility.

In the past, TiO_2 was considered to be a potentially low-cost feed for electrolysis, particularly if naturally occurring rutile could be used. In addition, a high-purity material, if required, could be prepared by acid extraction from ilmenite, an iron-titanium ore. However, TiO_2 has now lost this appeal. In recent years the preferred route to high-purity TiO_2 has been through oxidation of the tetrachloride rather than through hydrolysis of the sulfate, particularly when problems related to environmental control are taken into consideration (NMAB, 1972). Thus, titanium tetrachloride has become the lowest cost, high-purity feed material for electrolysis as well as that yielding by far the highest quality titanium metal.

D. Assessment of Alternative Routes

1. The halogen processes for the production of titanium metal have been studied rather exhaustively. The use of hydrogen as a reductant could work only at very high temperatures and, even then, the final product would be contaminated due to back reactions. The economics of achieving these higher temperatures and the necessity for recycle would prevent this route from being economical.

2. The titanium tetraiodide reaction, on the other hand, is limited by an equipment geometry problem. To date, the disproportionation takes place on an electrical filament that, as the titanium deposit grows, has a decreasing electrical resistance requiring higher amperage and lower voltage. If this problem can be avoided by unique design and the apparatus made of nonmetallic materials to prevent attack by the free iodine, the van Arkle route might be reexamined.

3. The process of reducing of titanium tetrachloride to the trichloride and its disproportionation involves an excessive number of separation and reaction steps that probably will prevent the process from ever developing past the laboratory stage.

4. In the area of metallothermic reductions, a process involving aluminum could be of interest. However, since $TiAl_3$ is a stable alloy, there could be excessive consumption of the reductant.

5. In the non-halide processes (i.e., those starting with titanium oxide and bypassing halogen intermediates), only calcium can successfully reduce the ultimate oxygen content below 1 percent. Accordingly, the alternate thermal routes do not appear competitive with the present Kroll process in terms of yield and purity of product.

6. The reduction-sulfidization of rutile followed by metallothermic reduction (magnesium) provides no important process benefits; in fact, it is more difficult to eliminate impurities in titanium by sulfidization than by the chloride route.

7. In electrolytic processes, the high deposition potential of titanium all but precludes electrowinning from either aqueous or organic electrolytes. Attempts at deposition from such baths indicate no promise of being successful by taking advantage of related factors such as hydrogen overvoltage considerations.

8. Electrolysis of $TiCl_4$ is severely handicapped by the need for physical separation of the cell into anolyte and catholyte compartments. Heretofore, attempts to use porous ceramics as a diaphragm have not been successful but the recent announcement of satisfactory operation of an intermediate sized cell with a long-lived diaphragm of novel design and construction offers renewed hope for this approach. The alternate expedient has been to use the deposit of titanium on a perforated cathode to compartment the cell.

Further research should be directed at the design and construction of diaphragms of long service life. Cells of higher capacity should be developed to take advantage of the potential for decreased labor costs.

9. Electrolysis of nonhalides in fused salts has not produced titanium of sufficient purity for good ductility and holds little promise of doing so. In addition, these materials at the purity required for cell feed are more costly than the tetrachloride.

10. Further consideration should be given to the electrolysis of TiO_2 in molten fluorides at temperatures above the melting point of titanium when satisfactory materials of construction are found.

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V. APPROACHES FOR FURTHER CONSIDERATION

In performing this study, the Panel undertook what were essentially three consecutive steps in its deliberations, each of which involved a review of the titanium process literature and discussions with experts in the field. First, the present commercial processes were reviewed and recent improvements were assessed, generally to determine what impact these might have on the purity and cost of the resultant sponge. Second, processes were reviewed that had been considered and studied in the laboratory state but had not been made commercial. This second step was to determine if any of these alternative processes had merit and should be studied further. Third, those that fit this latter criteria were considered for further study. This section describes such processes.

A. Modified Titanium Chloride Electrolysis

The deposition of high-quality titanium metal by electrolysis of titanium chlorides in fused salts requires that the titanium in solution be primarily in the form of the dichloride; the average Ti ion valence should be 2.2 or less (Leone et al., 1967). For processes in which titanium tetrachloride is fed to the electrolysis cells, the necessary valence adjustment and control can be accomplished by a cyclic operation involving alternate periods of feeding and deposition or by employing auxiliary cathodic elements operated at low current density so as to selectively reduce $TiCl_3$ to $TiCl_2$ (Myhren et al., 1968).

An alternate approach to achieving the low valence, proposed for consideration, involves partial reduction of $TiCl_4$ to $TiCl_2$ by reaction with sodium external to the cell and then feeding the resulting mixture of $TiCl_2$ and NaCl to an otherwise conventional titanium electrowinning cell. This partial reduction reaction is rapid and amenable to control (Homme et al., 1958). It can be performed as a continuous process (Wade, 1958) and is, in essence, the

first stage of the two-stage sodium reduction process of the RMI Co. A sodium reactor, by virtue of the rapid and continuous reaction, could supply feed to a number of titanium electrolysis cells.

B. Liquid Titanium Processes

In the previously discussed processes, the first titanium end product is sponge or crystals that must be consolidated by melting and alloying processes which are fairly complex. While the sponge costs from $1 to $1.45 per pound, the mill product in the form of sheets or plates can cost as much as $10 to $15 per pound after considerable machining. Obviously, a 20 to 30 percent reduction in the price of sponge will not reduce drastically the price of a sheet or plate of titanium or its alloys. To lower the price of titanium significantly and to make lower-cost titanium available for certain applications, the sponge (or crystal) and melting steps should be avoided. Probably savings of between 25 and 30 percent in energy and operating costs could be effected in a continuous liquid process through items such as obviating remelting, controlling the reaction vessel temperature, and continuity of flow.

Iron and aluminum, the two most commonly used structural materials, are produced and handled as a liquid that can be alloyed immediately and then cast into shapes by a continuous operation. Thus, if titanium is produced in a liquid form it probably could become a large volume structural material. Any process that produces liquid titanium must be a high-temperature process.

1. A Continuous High-Temperature Kroll Process

The present Kroll process reduces gaseous $TiCl_4$ with liquid magnesium at a temperature much below the melting point of Ti, which is $1667\,^{\circ}$C. Solid Ti is thus formed by contact with the vaporous $TiCl_4$ to give a sponge mass of Ti and $MgCl_2$. The resulting solid titanium sponge is removed from the reactor after shutdown and pulverized; the contained $MgCl_2$ is leached or vacuum distilled. The titanium powder then must be vacuum melted to form an ingot.

The total processing costs from sponge to ingot are a substantial part of the cost of titanium metal. By operating the reduction at temperatures above the melting point of titanium the sponge step may be eliminated. Full realization of the benefits would require the formation of pure Ti or specified alloys ready for fabrication without additional melting.

Halomet purports to have developed a continuous liquid titanium process capable of producing a titanium or titanium alloy ingot as an end product (Halomet, 1970; Othmer and Nowak, 1973). In the process, reduction of $TiCl_4$ by Mg is carried out above $1700^\circ C$. The reactor is electrically heated and operated under an argon atmosphere at a total pressure of 5 to 10 atmospheres. The reactor walls are water cooled, resulting in the formation of skull layers between the molten phases and the reactor wall. Since molten $MgCl_2$ floats on the molten titanium, the skull walls are, respectively, frozen $MgCl_2$ and Ti in the upper and lower portions of the reactor. The molten layers of $MgCl_2$ and Ti are removed through separate ports. The molten titanium is solidified under vacuum, resulting in the removal of residual Mg.

Two members of the Panel visited the Halomet plant in Germany during 1973; however, the plant was not in operation during either visit. Although the Panel did see samples of titanium produced by the process, no direct evidence of the successful continuous operation of the process was made available by Halomet.

A major problem in any high-temperature process is control and materials of construction. Skull melting requires close temperature control while complete melting requires special materials of construction. To the Panel's knowledge this process has not been proven in continuous operation.

2. High-Temperature Electrolytic Cell

The electrolytic concept for obtaining liquid titanium is being investigated now at the University of Cincinnati (Hoch, 1973). Some experiments

have been conducted using an electrolyte of barium chloride and fluoride containing some rare earth chlorides, and an anode feed of titanium oxide, chloride, or fluoride. The system is designed to operate at 1700° to 1725° C, just above the melting temperature of titanium. To minimize contamination by the solid walls, a Hoopes-type three-layer electrolytic cell arrangement is being tried. From the experiments conducted to date, apparently liquid titanium will float on top of the fluoride electrolyte.

C. Discussion

As a new approach to two-step titanium reduction technology, if the initial $TiCl_4$ is partially reduced to $TiCl_2$ by reaction with sodium external to the electrolysis cell, high-quality metal should be assured from fused-salt electrolysis when other operating conditions also are controlled satisfactorily. In addition, the production of titanium per unit of current passed should be doubled. Although this added benefit would be of major consequence, it must be balanced against a number of disadvantages: (1) since 2 mols of NaCl would accompany each mol of $TiCl_2$ fed to the titanium electrolysis cells, provision must be made for a gradual increase in electrolyte level and for periodic withdrawal of accumulated salt; (2) sodium electrolysis cells would be required to regenerate sodium and chlorine for recycle from the spent electrolyte; and (3) the feeding of substantial quantities of sodium chloride coupled with the regeneration of the sodium would preclude the use of eutectic melts that, by virtue of their lower melting temperatures, tend to alleviate materials of construction problems.

If the liquid titanium processes mentioned previously become a reality, the cost of titanium should decrease substantially by elimination of the intermediate sponge. These processes could operate in relatively small equipment, because they are continuous. However, the continuous Kroll, (i.e., Halomet process) requires a minimum size for the reaction vessel so that heat losses are minimal. The exothermic heat of reaction is important in maintaining the system in the liquid state.

The major problem with liquid titanium processes is the containment of molten titanium. No available nitride, carbide, or oxide material is thermodynamically stable enough to permit contact with liquid titanium at its melting point for any length of time. An exception may be the rare earth oxides and yttrium oxide (Y_2O_3) or combinations that potentially have better properties (Hoch, 1973).

An alternative solution to the materials problem is the use of a skull formed by balanced heat flow in the system. This is suggested in the Halomet process but the successful use of such a skull for extended periods of time has not been demonstrated. The development of a refractory material for containing molten titanium requires a major material breakthrough and thus, is, less likely than the use of a skull for this purpose.

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